CHAPTER 1

INTRODUCTION

1.1. QUANTUM MECHANICS

The branch of Physics which deals with the properties of matter that is position, momentum and energy etc. on atomic and subatomic level is called quantum mechanics.

The word quantum is a Latin word means small amount or bundle. The plural of quantum is quanta. On atomic and sub atomic level dynamical properties of body have some discrete values with some integral multiple. For example energy of photons is $E = nhf$

1.2. Difference between quantum Mechanics and Classical Mechanics

Quantum mechanics differs with classical mechanics on the basis of following parameters

a) By size

Classical mechanics deals with molecular size and relatively slow particles that is classical mechanics deals macroscopic particles while on the other hand quantum mechanics deals microscopic particles, slow as well as fast both atomic and sub atomic levels.

b) Certain and Uncertain

Classically properties such as position, momentum, energy and time etc. are known or certain with accuracy and precession. While quantum mechanically these properties are dealt statistically and are uncertain.

c) UV catastrophe

We know that black body absorbs and emits all type of radiations. Raleigh and Jean, classically explained the black body radiations spectrum

The Raleigh and Jean's relation about the spectral radiancy or radiation density was

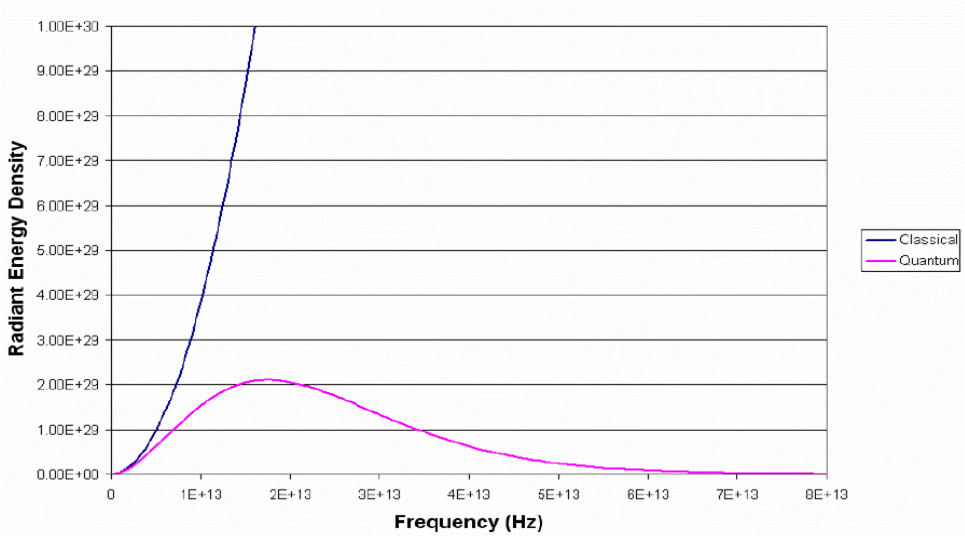
$$Udv = \frac{8hkT}{c^3}v^2 dv$$

Here Udv is spectral radiancy or radiation density. If we increase the frequency (v) to infinity, the spectral radiancy Udv also becomes infinite. But experimentally, it is observed that as v becomes infinity that is moving toward ultraviolet region, the spectral radiancy Udv become zero.

So, classical explanation of black body radiation failed. This is called UV catastrophe.

Quantum mechanically, Plank derived a relation about spectral radiancy. That relation satisfied both theoretical as well as experimental results. His relation was

$$Udv = \frac{8\pi h\nu^3}{c^3 e^{\frac{h\nu}{kT}-1}} dv$$



d) Photoelectric effect

Classically it was stated that photoelectric effect can take place at any frequency and at any intensity of incident light falling on a metal plate but experimentally it was found incorrect. Maxwell quantum mechanically explained that below threshold frequency of incident light, no photo electron emits from the metal surface. Similarly experimentally it is verified that below thresh hold frequency, emission of photoelectrons do not depend on the intensity of light. Maxwell relation is

$$hf = hf_o + K.E$$

Here f is the frequency of incident light, f_o is threshold frequency and K.E is the kinetic energy of photo electrons.

e) Compton's Effect

Classically, light cannot produce collisions or scattering. It can only produce interference, diffraction and polarization etc. so Compton's effect cannot be explained classically. Quantum

mechanically, Compton's effect can be explained successfully by considering the particle nature of light that is photon.

f) Particle tunneling

Classically a material particle cannot tunnel through a barrier but quantum mechanically a particle can tunnel through a barrier. For example tunneling of alpha through nucleus and tunneling of electrons and holes through potential barrier in semiconductor diode.

g) Particle Diffraction

Classically diffraction of particles that is diffraction of electrons, protons neutrons etc. cannot be explained but quantum mechanically, particles diffraction experiments such as Davisson and Germer's experiment and double slit electron diffraction etc. can be explained easily.

h) Spectroscopy

Classical theory gives continuous spectrum of an atom which is against the experimental evidences, but quantum mechanics gives discrete spectrum of an atom which supports the experimental results.

i) Molar specific heat at constant volume

Classically the relation of molar specific heat at constant volume is given as

$$c_v = 3R$$

Here R is universal gas constant.

This equation holds good at higher temperatures but when we decrease the temperature very low, this equation fails.

Maxwell quantum mechanically explained the molar specific heat at constant volume both for high as well as low temperatures .His relation is

$$c_v = \frac{g\pi N_A k}{5}\left(\frac{kT}{h\nu}\right)^2$$

1.3. WAVE FUNCTION

We know that the information about the sound waves comes from the pressure changes in the medium. The velocity of the sound wave is given by the relation

$$v = \sqrt{\frac{P}{\rho}}$$

Here P is the pressure of the medium and ρ is the density of the medium. The information about the electromagnetic waves is obtained from the changes of electric and magnetic fields, The velocity of electromagnetic waves is given by the relation

$$c = \frac{1}{\sqrt{\mu_o \epsilon_o}}$$

Here $\mu_o \ and \ \epsilon_o$ are the permeability and the permittivity of the free space respectively.

The information about the transverse waves can be obtained from the tension changes.

The velocity of the transverse waves along string is given by

$$v = \sqrt{\frac{T \times l}{m}}$$

Here T is the tension in the string, l is the length of the string and m is the mass of the string.

The information about the water waves can be obtained by the height of the water wave. The velocity of water wave is given by

$$v = \sqrt{gh}$$

Here g is acceleration due to gravity and h is the height of the wave.

Quantum mechanically according to De-Broglie, matter also acts as a wave called matter wave.

The information about the matter wave is obtained by the wave function. Wave function generally represented by ψ. here ψ is the function of position and time.

That is $\psi = \psi(r, t) = \psi(x, y, z, t)$

ψ may be real or complex.

RESTRICTIONS ON ψ

1. ψ should be single valued and continuous. Single value means, ψ should have a specific value at a specific position and a specific time. Continuous means there will be no sudden changes in motion of the wave.

2. Derivatives of ψ that is $\frac{d\psi}{dx}$ or $\frac{d^2\psi}{dx^2}$should be continuous and single valued.

3. The information about the matter wave cannot be obtained only evaluating the ψ But

$\psi^* \psi = |\psi|^2$ called probability density gives information. Here ψ^* Is the complex conjugate of ψ.

ψ can be complex but $\psi^* \psi = |\psi|^2$ is always real.

4. ψ should be normalized. That is

$$\int_{-\infty}^{+\infty} \psi^* \psi dv = 1 or\ 0$$

1 means probability of the existence of the particle in this given volume is 100%.

0 means there is no probability of the existence of the particle in this given volume.

Intermediate probabilities that is if

$$\int_{-\infty}^{+\infty} \psi^* \psi dv = 0.3$$

Means there are 30% chances.

$$\int_{-\infty}^{+\infty} \psi^* \psi dv = 0.5$$

Means there are 50% chances.

5. Ψ should be linear. It means if ψ_1 and ψ_2 are the solutions of ψ then

$$\psi = a\psi_1 + b\psi_2$$

Here *a* and *b* are the constants.

1.4. MATTER WAVE EQUATION

Consider a matter wave is moving along x-axis with velocity v .It covers distance dx in time dt. Then $v = \frac{dx}{dt}$

Or $dx = vdt$

If ψ (x,t) is the wave function which describe the behavior of this matter wave then we can write

$$\frac{d\psi}{dx} = \frac{d\psi}{vdt}$$

Similarly

$$\frac{d^2\psi}{dx^2} = \frac{d}{vdt}\frac{d\psi}{vdt}$$

$$\frac{d^2\psi}{dx^2} = \frac{1}{v^2}\frac{d^2\psi}{dt^2}$$

This is the equation of matter wave. This is second order differential equation whose solution is

$$\psi = Ae^{-i\omega(t-\frac{x}{v})}$$

Here A is the amplitude of the wave and ω is the angular frequency.

PHASE VELOCITY

Velocity of the single matter wave is called Phase velocity.

It is represented by V_p

And $V = f\lambda$

Here f is the frequency of the wave and λ is the wave length.

According to De-Broglie $P = \frac{h}{\lambda}$

$$\lambda = \frac{h}{P} \quad \text{----------1}$$

According to Einstein

$E=mc^2$ ----------2

By plank

E=hf ----------3

Comparing 2 and 3

$$hf=mc^2$$

$$f = \frac{mc^2}{h} \text{ ----------4}$$

Substitute the values of λ and f in equation of phase velocity.

$$v_p = \frac{mc^2}{h}\frac{h}{p}$$

$$v_p = \frac{mc^2}{mv} = \frac{c^2}{v}$$

As v<c, so this equation shows V_p>c. That is phase velocity can be increased by speed of light.

Now as c=f λ this gives $c = \frac{\omega\lambda}{2\pi}$

$$v_p = \frac{\omega^2\lambda^2}{v4\pi^2} = \frac{\omega^2\lambda^2}{\frac{\lambda}{2\pi}4\pi^2} = \frac{\omega}{\frac{\lambda}{2\pi}} = \frac{\omega}{k}$$

Here ω is angular frequency and k is wave number.

GROUP VELOCITY

It is observed that generally a single matter wave does not move but a group of matter waves having different wave lengths and frequency move together. The velocity of this group of waves or wave packets is called group velocity.

It is represented by V_g and

$$v_g = \frac{d\omega}{dk}$$

In special case for light waves V_p=V_g

Now

$$v_g = df d\lambda$$

$$v_g = \frac{d\omega d\lambda}{2\pi}$$

$$v_g = \frac{d\omega}{dk}$$

CHAPTER 2

WAVE MECHANICAL CONCEPTS

SCHRODINGER'S WAVE EQUATION

Schrodinger derived an equation for the matter wave which has same role in quantum mechanics as Newton's second law in classical mechanics. Schrodinger derived matter wave equation both for time dependent and time independent modes.

SCHRODINGER'S TIME DEPENDENT EQUATION

Consider a matter wave is moving along x=axis with velocity v. The wave function of this wave is

$$\psi = Ae^{-i\omega(t-\frac{x}{v})}$$

As $\omega = 2\pi f$

So $\psi = Ae^{-i2\pi f(t-\frac{x}{v})}$

$$\psi = Ae^{-i2\pi(ft-\frac{fx}{v})}$$

As $E = hf$

So $\psi = Ae^{-i2\pi(\frac{Et}{h}-\frac{fx}{f\lambda})}$

Also $p = \frac{h}{\lambda}$

$$\psi = Ae^{-i2\pi(\frac{Et}{h}-\frac{px}{h})}$$

$$\psi = Ae^{\frac{-i2\pi}{\hbar}(Et-px)}$$

$$\psi = Ae^{\frac{-i}{\hbar}(Et-px)} \quad \text{----------1}$$

Differentiate equation 1 with respect to x

$$\frac{\partial\psi}{\partial x} = \frac{ip}{\hbar}Ae^{\frac{-i}{\hbar}(Et-px)} \quad \text{----------2}$$

Differentiate equation 2 with respect to x

$$\frac{\partial^2\psi}{\partial x^2} = \frac{-p^2}{\hbar^2}Ae^{\frac{-i}{\hbar}(Et-px)}$$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{-p^2\psi}{\hbar^2}$$

$$p^2\psi = -\hbar^2\frac{\partial^2\psi}{\partial x^2} \text{----------3}$$

Differentiate equation 1 with respect to t

$$\frac{\partial\psi}{\partial t} = \frac{-iE}{\hbar}Ae^{\frac{-i}{\hbar}(Et-px)}$$

$$E\psi = i\hbar\frac{\partial\psi}{\partial t} \text{----------4}$$

If E is the total energy then

$$E = T + U$$

Here T is kinetic energy and U is potential energy.

Now above equation can be written as

$$E = \frac{P^2}{2m} + U$$

Multiply both sides by ψ

$$E\psi = \frac{P^2\psi}{2m} + U\psi$$

Substitute the values of $E\psi \; and \; p^2\psi$

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + U\psi$$

This is one dimensional time dependent Schrodinger's equation.

For three dimensions

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + U\psi$$

$$\frac{-\hbar^2\nabla^2\psi}{2m} + U\psi = i\hbar\frac{\partial\psi}{\partial t}$$

Here $$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

Schrodinger's time independent equation

Consider a matter wave is moving along x-axis with velocity v. The wave function of this wave is

$$\psi = Ae^{-i\omega(t-\frac{x}{v})}$$

As $$\omega = 2\pi f$$

So $$\psi = Ae^{-i2\pi f(t-\frac{x}{v})}$$

$$\psi = Ae^{-i2\pi(ft-\frac{fx}{v})}$$

As $$E = hf$$

So $$\psi = Ae^{-i2\pi(\frac{Et}{\hbar}-\frac{fx}{f\lambda})}$$

Also $$P = \frac{h}{\lambda}$$

$$\psi = Ae^{-i2\pi(\frac{Et}{\hbar}-\frac{Px}{\hbar})}$$

$$\psi = Ae^{\frac{-i2\pi}{\hbar}(Et-Px)}$$

$$\psi = Ae^{\frac{-i}{\hbar}(Et-Px)} \quad \text{----------1}$$

This equation can be written as

$$\psi = Ae^{\frac{iPx}{\hbar}}e^{\frac{-iEt}{\hbar}}$$

$$\psi = Ae^{\frac{iPx}{\hbar}}\phi(t) \quad \text{----------2}$$

Here $\phi(t) = e^{\frac{-iEt}{\hbar}}$

Differentiate equation 2 with respect to x

$$\frac{\partial\psi}{\partial x} = \frac{iP}{\hbar}Ae^{\frac{ipx}{\hbar}}\phi(t) \quad \text{----------3}$$

Differentiate equation 3 with respect to x

$$\frac{\partial^2\psi}{\partial x^2} = \frac{-P^2}{\hbar^2}Ae^{\frac{ipx}{\hbar}}\phi(t)$$

$$\frac{\partial^2\psi(x)}{\partial x^2}\phi(t) = \frac{-P^2\psi(x)\phi(t)}{\hbar^2}$$

As $\psi = \psi(x)\phi(t)$

$$p^2\psi(x) = -\hbar^2\frac{\partial^2\psi(x)}{\partial x^2} \quad \text{----------4}$$

If E is the total energy then

$$E = T + U$$

Here T is kinetic energy and U is potential energy.

Now above equation can be written as

$$E = \frac{p^2}{2m} + U$$

Multiply both sides by ψ(x)

$$E\psi(\mathrm{x}) = \frac{p^2\psi(\mathrm{x})}{2m} + U\psi(\mathrm{x})$$

Substitute the value of $p^2\psi$(x)

$$E\psi(\mathrm{x}) = \frac{-\hbar^2}{2m}\frac{\partial^2\psi(\mathrm{x})}{\partial x^2} + U\psi(\mathrm{x})$$

This is one dimensional time independent Schrodinger's equation.

For three dimensions

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + U\psi = E\psi(\mathrm{x})$$

$$\frac{-\hbar^2\nabla^2\psi(\mathrm{x})}{2m} + U\psi(\mathrm{x}) = E\psi(\mathrm{x})$$

$$\nabla^2\psi(\mathrm{x}) + \frac{2m}{\hbar^2}(E - U)\psi(\mathrm{x}) = 0$$

Here $$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

Limitations of Schrodinger's Equation

1. This equation is not dimensionally consistent. It has first order time derivative and second order position derivative.
2. It is only for non-relativistic particles.
3. It is only valid for low energy particles. For high energy particles this equation is not valid.
4. The pair production. Annihilation of matter and antimatter etc. cannot be explained by Schrodinger's equation.

Probability Current density Or Equation of continuity

One dimensional time dependent Schrodinger's equation is

$$i\hbar\frac{\partial\psi}{\partial t}=\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+U\psi\text{------ (1)}$$

We take its complex conjugate

$$-i\hbar\frac{\partial\psi^*}{\partial t}=\frac{-\hbar^2}{2m}\frac{\partial^2\psi^*}{\partial x^2}+U\psi^*\text{------ (2)}$$

Multiply equation 1 with ψ^* and equation 2 with ψ and subtract.

$$i\hbar\psi^*\frac{\partial\psi}{\partial t}+i\hbar\psi\frac{\partial\psi^*}{\partial t}=\frac{-\hbar^2}{2m}\psi^*\frac{\partial^2\psi}{\partial x^2}+U\psi^*\psi+\frac{-\hbar^2}{2m}\psi\frac{\partial^2\psi^*}{\partial x^2}-U\psi\psi^*$$

$$i\hbar\frac{\partial(\psi\psi^*)}{\partial t}=\frac{-\hbar^2}{2m}\frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x}-\psi\frac{\partial\psi^*}{\partial x}\right)$$

$$\frac{\hbar}{2im}\frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x}-\psi\frac{\partial\psi^*}{\partial x}\right)+\frac{\partial(\psi\psi^*)}{\partial t}=0$$

$$\frac{\partial J}{\partial x}+\frac{\partial\rho}{\partial t}=0$$

This is equation of continuity. Here $\rho=\psi\psi^*$ is called probability density and

$J=\frac{\hbar}{2im}\left(\psi^*\frac{\partial\psi}{\partial x}-\psi\frac{\partial\psi^*}{\partial x}\right)$ is called probability current density.

For three dimension

$$\nabla.J+\frac{\partial\rho}{\partial t}=0$$

Now $$J=\frac{\hbar}{2im}(\psi^*\nabla\psi-\psi\nabla\psi^*)$$

Applications of Schrodinger's Equation

1. Particle in a box

Or trapped particle

Or Particle in an infinite potential well

Or Particle in an infinite potential box

Or Schrodinger's cat problem

Consider a particle of mass m is trapped in a box of length L. inside the box potential energy is zero. That is particle can move freely inside the box. The walls of box have infinite potential. So that particle cannot escape from the walls.

Simply we can write the restrictions as

$$U = 0 \qquad for\ \ 0 < x < L$$

$$U = \infty \qquad for\ \ L \leq x \leq 0$$

This is one dimensional time independent problem. So we solve Time independent Schrodinger's equation.

$$\frac{\mathrm{d}^2\psi(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}(E - U)\psi(\mathrm{x}) = 0$$

As inside the box u=o

So Schrodinger's equation will become

$$\frac{\mathrm{d}^2\psi(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}E\psi(\mathrm{x}) = 0$$

$$\frac{\mathrm{d}^2\psi(\mathrm{x})}{dx^2} + k^2\psi(\mathrm{x}) = 0 \quad \text{----------1}$$

This is second order differential equation. Here $k^2 = \frac{2mE}{\hbar^2}$

The solution of equation 1 is

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

Or

$$\psi(x) = A\sin kx + B\cos kx \text{----------2}$$

Here A and B are constants whose values can be found by boundary conditions.

At boundaries $x = 0 \;\; and \; x = L \;\; \psi(x) = 0$

Use these values in equation 2

$$0 = A \sin 0 + B \cos 0$$

This gives B=0

So Acceptable solution will be

$$\psi(x) = A \sin kx$$

$$\psi(x) = A \sin \frac{\sqrt{2mE}}{\hbar} x$$

Energy of the Particle in the Box

As the wave function inside the box is

$$\psi(x) = A \sin \frac{\sqrt{2mE}}{\hbar} x$$

At boundary $x = L \;\; \psi(x) = 0$ so

$$0 = A \sin \frac{\sqrt{2mE}}{\hbar} L$$

$$\frac{\sqrt{2mE}}{\hbar} L = \sin^{-1} 0 = n\pi$$

$$\sqrt{2mE} = \frac{n\pi\hbar}{L}$$

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

This is the energy of the particle inside the box. This equation shows that inside the box energy of the particle is quantized.

For first level n=1

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2}$$

For second level n=2

$$E_2 = \frac{2\pi^2 \hbar^2}{mL^2}$$

And so on.

Normalized Wave function

For normalized condition

$$\int_{-\infty}^{+\infty} \psi^* \psi dv = 1 or\ 0$$

Here inside the box

$$\int_0^L \psi^* \psi dx = 1$$

$$\int_0^L (A \sin kx)(A \sin kx)\, dx = 1$$

$$\int_0^L A^2 \sin^2 kx\, dx = 1$$

As $\sin^2 kx = \frac{1-\cos 2kx}{2}$

$$A^2 \int_0^L \frac{1-\cos 2kx}{2} dx = 1$$

$$\frac{A^2}{2}\left[\int_0^L dx - \int_0^L \cos 2kx\, dx\right] = 1$$

$$\frac{A^2}{2}\left[|x|_0^L - \left|\frac{\sin 2kx}{2k}\right|_0^L\right] = 1$$

As $k = \frac{n\pi}{L}$

$$\frac{A^2}{2}\left[L - \frac{\sin 2kL}{2k} + \sin 0\right] = 1$$

$$\frac{A^2}{2}\left[L - \frac{\sin 2\frac{n\pi}{L}L}{2\frac{n\pi}{L}}\right] = 1$$

$$\frac{A^2}{2}\left[L - \frac{\sin 2n\pi}{2\frac{n\pi}{L}}\right] = 1$$

As $\sin 2n\pi = 0$

$$\frac{A^2}{2}[L] = 1$$

So $$A = \sqrt{\frac{2}{L}}$$

So normalized wave function will be

$$\psi(x) = \sqrt{\frac{2}{L}}\sin kx$$

Or $$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{\sqrt{2mE}}{\hbar}x$$

2. Schrodinger equation for finite potential box

Or Schrodinger's equation for the finite potential well

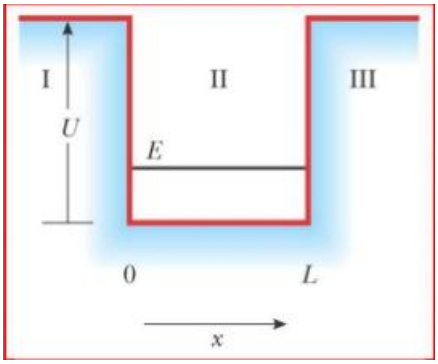
Or Schrodinger's wave equation for square well potential

In real world, infinite potential well or box does not exist but there are almost all wells or box are of finite potential.

Now we consider a finite potential box of length. Inside the box u=0. So inside the box particle can move freely. Outside the box u≠0 so in this region the motion of the particle will be constrained.

Above conditions can be written as

$$u = \begin{cases} 0 & 0 < x < L \\ u & L \leq x \leq 0 \end{cases}$$



Now we consider three regions **I**, **ii** and **iii**

Classically when energy E of the particle will be greater than the potential energy u of the region I and iii ,particle can easily move in all three regions. If E<U then particle cannot move in regions i and iii.

But quantum mechanically If E<U then there will be a probability of the particle to escape the walls of the box. Now we take this case that is E<U and solve Schrodinger's wave equation for all the three regions.

Schrodinger's equation for the region I

We take one dimensional time independent Schrodinger's equation and solve it for the condition E<U

$$\frac{\mathrm{d}^2\psi_1(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}(E-U)\psi_1(\mathrm{x}) = 0$$

As E<U so

$$\frac{\mathrm{d}^2\psi_1(\mathrm{x})}{dx^2} - \frac{2m}{\hbar^2}(U-E)\psi_1(\mathrm{x}) = 0$$

$$\frac{\mathrm{d}^2\psi_1(\mathrm{x})}{dx^2} - a^2\psi_1(\mathrm{x}) = 0$$

$$\text{Here } a^2 = \frac{2m}{\hbar^2}(U-E)$$

Above equation is a second order differential equation whose acceptable solution will be

$$\psi_1(\mathrm{x}) = e^{ax}$$

Schrodinger's equation for the region II

We take one dimensional time independent Schrodinger's equation and solve it for the condition E<U

$$\frac{\mathrm{d}^2\psi_{11}(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}(E-U)\psi_{11}(\mathrm{x}) = 0$$

Here U=0 so

$$\frac{\mathrm{d}^2\psi_{11}(\mathrm{x})}{dx^2} + \frac{2mE}{\hbar^2}\psi_{11}(\mathrm{x}) = 0$$

$$\frac{\mathrm{d}^2\psi_{11}(\mathrm{x})}{dx^2} + k^2\psi_{11}(\mathrm{x}) = 0$$

Here $k^2 = \frac{2mE}{\hbar^2}$

Above equation is a second order differential equation whose acceptable solution will be

$$\psi_{11}(\mathrm{x}) = Ae^{ikx} + Be^{-ikx}$$

Schrodinger's equation for the region III

We take one dimensional time independent Schrodinger's equation and solve it for the condition E<U

$$\frac{\mathrm{d}^2\psi_{111}(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}(E-U)\psi_{111}(\mathrm{x}) = 0$$

Here E<U so

$$\frac{\mathrm{d}^2\psi_{111}(\mathrm{x})}{dx^2} - \frac{2m}{\hbar^2}(U-E)\psi_{111}(\mathrm{x}) = 0$$

$$\frac{\mathrm{d}^2\psi_{111}(\mathrm{x})}{dx^2} - a^2\psi_{111}(\mathrm{x}) = 0$$

Here $a^2 = \frac{2m}{\hbar^2}(U-E)$

Above equation is a second order differential equation whose acceptable solution will be

$$\psi_{111}(\mathrm{x}) = e^{-ax}$$

Complete Solution

$$\psi = \psi_1(\mathrm{x}) + \psi_{11}(\mathrm{x}) + \psi_{111}(\mathrm{x})$$

$$\psi = e^{ax} + Ae^{ikx} + Be^{-ikx} + e^{-ax}$$

Energy of the particle inside box

As $k^2 = \frac{2mE}{\hbar^2}$

$$E = \frac{k^2\hbar^2}{2m}$$

As $k = n\pi$ so

$$E = \frac{n^2\pi^2\hbar^2}{2m}$$

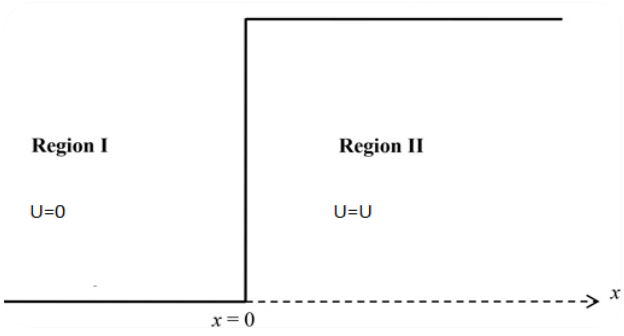
3. Schrodinger's equation for step potential

Or Finite potential step

Consider a beam of slow particles or a single particle is coming from a region where potential U=0 and entre in a region by taking a step where U≠ 0

So restrictions can be written as

$$U = \begin{cases} o & x < 0 \\ U & x \geq 0 \end{cases}$$



It is one dimensional problem

We solve time independent Schrodinger's equation for both regions.

Schrodinger's equation for the region 1

$$\frac{\mathrm{d}^2\psi_1(\mathrm{x})}{dx^2}+\frac{2m}{\hbar^2}(E-U)\psi_1(\mathrm{x})=0$$

For region 1 U=o

So Schrodinger's equation will become

$$\frac{\mathrm{d}^2\psi_1(\mathrm{x})}{dx^2}+\frac{2m}{\hbar^2}E\psi_1(\mathrm{x})=0$$

$$\frac{\mathrm{d}^2\psi_1(\mathrm{x})}{dx^2}+{k_1}^2\psi_1(\mathrm{x})=0 \quad \text{----------1}$$

This is second order differential equation. Here ${k_1}^2=\frac{2mE}{\hbar^2}$

The solution of equation 1 is

$$\psi_1(x)=e^{ik_1x}+re^{-ik_1x}$$

Here e^{ik_1x} incident wave and re^{-ik_1x} reflected wave.

r is the amplitude of reflected wave also called coefficient of reflection.

Schrodinger's equation for the region 11

$$\frac{\mathrm{d}^2\psi_{11}(\mathrm{x})}{dx^2}+\frac{2m}{\hbar^2}(E-U)\psi_{11}(\mathrm{x})=0$$

Here For region 11 U=U(x)

$$\frac{\mathrm{d}^2\psi_{11}(\mathrm{x})}{dx^2}+{k_2}^2\psi_{11}(\mathrm{x})=0 \quad \text{----------2}$$

This is second order differential equation. Here ${k_2}^2=\frac{2m(E-U)}{\hbar^2}$

The solution of equation 2 is

$$\psi_{11}(x)=te^{ik_2x}+e^{-ik_2x}$$

The acceptable solution will be

$$\psi_{11}(x)=te^{ik_2}$$

t is the amplitude of transmission wave. t is also called coefficient of transmission.

Values of r and t

In order to find the values of r and t we apply boundary condition.

At x=0 $\psi_1(x) = \psi_{11}(x)$

This means $e^{ik_1x} + re^{-ik_1x} = te^{ik_2x}$

$$e^{ik_1 0} + re^{-ik_1 0} = te^{ik_1 0}$$

1+r=t ---------- (A)

Similarly at x=0

$$\frac{\partial \psi_1}{\partial x} = \frac{\partial \psi_{11}}{\partial x}$$

$$ie^{ik_1x} - ik_1re^{-ik_1x} = ik_2te^{ik_2x}$$

$$ik_1e^{ik_1 0} - ik_1re^{-ik_1 0} = ik_2te^{ik_2 0}$$

$$ik_1 - ik_1r = itk_2$$---------- (B)

Use value of t from equation A in equation B

$$ik_1 - ik_1r = i(1+r)k_2$$

$$k_1 - k_1r = k_2 + rk_2$$

$$(k_1 + k_2)r = k_1 - k_2$$

$r = \frac{k_1 - k_2}{(k_1 + k_2)}$ ----------(c)

Now substitute value of r in equation B

$$k_1 - \frac{k_2 - k_1}{(k_1 + k_2)} = tk_2$$

$t = \frac{2k_1}{(k_1 + k_2)}$ ---------- (D)

Reflectivity

The probability of reflection is called reflectivity. It is represented by R.

$$R = |r|^2$$

$$R = \left(\frac{k_1 - k_2}{(k_1 + k_2)}\right)^2$$

Transmitivity

The probability of transmission is called transmitivity. It is represented by T.

$$T = |t|^2$$

$$T = \left(\frac{2k_1}{(k_1 + k_2)}\right)^2$$

R+T=?

Now we have to show that at boundary R+T=?

$$R + T = \left(\frac{k_1 - k_2}{(k_1 + k_2)}\right)^2 + \left(\frac{2k_1}{(k_1 + k_2)}\right)^2$$

At boundary $k_1 \approx k_2$

So $$R + T = \left(\frac{k_2 - k_2}{(k_1 + k_2)}\right)^2 + \left(\frac{2k_2}{(k_2 + k_2)}\right)^2$$

$$R + T = 0 + \left(\frac{2k_2}{(k_2 + k_2)}\right)^2$$

So $$R + T = 1$$

Potential barrier

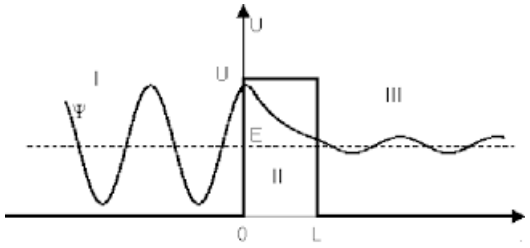
Barrier tunneling

Or tunneling effect

Consider a beam of particles or a particle of mass m and energy E comes from a region where potential is zero. On the way it strike a potential barrier of height U. classically, if E>U the particle can cross the barrier but if E<U then particle cannot cross the barrier. Quantum mechanically there is a probability of the particle to transmit the barrier. This is called tunneling effect. Now we solve quantum mechanically Schrodinger's equation for this tunneling effect.

We take three regions 1, 11 and 111 such that

$$U(x) = \begin{cases} 0 & x < 0 \\ 0 & x > 0 \\ U & 0 \le x \le L \end{cases}$$



Here L is the width of barrier and U is the strength of barrier.

Schrodinger's equation for the region 1

$$\frac{\mathrm{d}^2\psi_1(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}(E-U)\psi_1(\mathrm{x}) = 0$$

For region 1 U=o

So Schrodinger's equation will become

$$\frac{\mathrm{d}^2\psi_1(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}E\psi_1(\mathrm{x}) = 0$$

$$\frac{\mathrm{d}^2\psi_1(\mathrm{x})}{dx^2} + {k_1}^2\psi_1(\mathrm{x}) = 0 \quad \text{----------1}$$

This is second order differential equation. Here ${k_1}^2 = \frac{2mE}{\hbar^2}$

The solution of equation 1 is

$$\psi_1(x) = e^{ik_1x} + re^{-ik_1x}\text{----------2}$$

Here e^{ik_1x} incident wave and re^{-ik_1x} reflected wave. Here r is the amplitude of reflected wave also called coefficient of reflection.

Schrodinger's equation for the region 11

$$\frac{\mathrm{d}^2\psi_{11}(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}(E-U)\psi_{11}(\mathrm{x}) = 0$$

Here For region 11 U=U and E<U

$$\frac{\mathrm{d}^2\psi_{11}(\mathrm{x})}{dx^2} - \frac{2m}{\hbar^2}(U-E)\psi_{11}(\mathrm{x}) = 0$$

$$\frac{\mathrm{d}^2\psi_{11}(\mathrm{x})}{dx^2} - {k_2}^2\psi_{11}(\mathrm{x}) = 0\text{----------3}$$

This is second order differential equation. Here ${k_2}^2 = \frac{2m(U-E)}{\hbar^2}$

The solution of equation 3 is

$$\psi_{11}(x) = Ae^{k_2x} + Be^{-k_2x}\text{----------4}$$

Schrodinger's equation for the region 111

$$\frac{\mathrm{d}^2\psi_{111}(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}(E-U)\psi_{111}(\mathrm{x}) = 0$$

For region 111 U=o

So Schrodinger's equation will become

$$\frac{\mathrm{d}^2\psi_{111}(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}E\psi_{111}(\mathrm{x}) = 0$$

$$\frac{\mathrm{d}^2\psi_{111}(\mathrm{x})}{dx^2} + {k_1}^2\psi_{111}(\mathrm{x}) = 0 \quad \text{----------5}$$

This is second order differential equation. Here ${k_1}^2 = \frac{2mE}{\hbar^2}$

The solution of equation 5 is

$$\psi_{111}(x) = te^{ik_1x} + e^{-ik_1x}$$

Here the acceptable solution iste^{ik_1x}.

So $$\psi_{111}(x) = te^{ik_1x}$$----------6

Here t is the amplitude of transmitted wave also called coefficient of transmission.

Total wave function

$$\psi = \psi_1 + \psi_{11} + \psi_{111}$$

$$\psi = e^{ik_1x} + re^{-ik_1x} + Ae^{k_2x} + Be^{-k_2x} + te^{ik_1x}$$

Quantum mechanical Harmonic oscillator

Harmonic oscillator is a body which vibrates about equilibrium position. For example mass spring system. Consider a one dimensional harmonic oscillator which is vibrating along x=axis. According to Hook's law force will be

$$F = -kx$$ ----------1

Here K is hook's constant.

Also according to Newton's law

$$F = m\frac{d^2x}{dt^2}$$ ----------2

Comparing 1 and 2

$$m\frac{d^2x}{dt^2} = -kx$$

$$\frac{d^2x}{dt^2} = -\frac{k}{m}x$$

$$\frac{d^2x}{dt^2} = -\omega^2x$$ ----------3

This is called equation of simple harmonic oscillation. Here ω^2 is constant.

Now if U is potential energy then we know that

$$u = -\int F dx$$

$$u = -\int -kx dx$$

$$u = \frac{1}{2}kx^2 \text{----------4}$$

Now we solve one dimensional time independent Schrodinger's equation.

$$\frac{\mathrm{d}^2\psi(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}(E - U)\psi(\mathrm{x}) = 0$$

$$\frac{\mathrm{d}^2\psi(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}(E - \frac{1}{2}kx^2)\psi(\mathrm{x}) = 0$$

$$\frac{\mathrm{d}^2\psi(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}(E - \frac{1}{2}kx^2)\psi(\mathrm{x}) = 0$$

In order to solve this equation we put

$$\beta = \frac{2mE}{\hbar^2\alpha},\ \alpha^2 = \frac{mk}{\hbar^2} \text{ and } y = x\alpha^{\frac{1}{2}}$$

Here α and y are dimensionless constants. So above equation can be written as

$$\frac{\mathrm{d}^2\psi(\mathrm{y})}{dy^2} + (\alpha - y^2)\psi(\mathrm{y}) = 0$$

If $\alpha \ll y$ then $\alpha \to 0$

So

$$\frac{\mathrm{d}^2\psi(\mathrm{y})}{dy^2} - y^2\psi(\mathrm{y}) = 0$$

$$(\frac{\mathrm{d}^2}{dy^2} - y^2)\psi(\mathrm{y}) = 0$$

$$(\frac{\mathrm{d}}{dy} + y)(\frac{\mathrm{d}}{dy} - y)\psi(\mathrm{y}) = 0$$

$$(\frac{\mathrm{d}}{dy} + y)\psi(\mathrm{y}) = 0$$

$$\frac{d\psi}{\psi} = -ydy$$

Integrate both sides

$$\int \frac{d\psi}{\psi} = -\int ydy$$

$$\ln \psi = -\frac{y^2}{2}$$

$$\psi = \phi e^{-\frac{y^2}{2}}$$

Here ϕ is called Hermite polynomial. The complete solution will be

$$\psi_n = \left(\frac{2mE}{\hbar}\right)^{\frac{1}{4}} (2^n n!)^{-\frac{1}{2}} H_n(y) e^{-\frac{y^2}{2}}$$

Energy Eigen values of harmonic oscillator

As $\alpha = \frac{2E}{\hbar\omega}$ this is only true if $\alpha = 2n + 1$

So $$\frac{2E}{\hbar\omega} = 2n + 1$$

$$E_n = (2n + 1)\frac{\hbar\omega}{2}$$

$$E_n = (n + \frac{1}{2})\hbar\omega$$

Here $n = 0,1,2 - - - - -$

Above equation is energy Eigen values of harmonic oscillator. For ground state $n = 0$.

So

$$E = \frac{1}{2}\hbar\omega$$

This is called zero point energy. This states that at mean position harmonic oscillator has some energy not equal to zero.

CHAPTER 3

GENRAL FORMALISM OF QUANTUM MECHANICS

Postulates of Quantum Mechanics

On the Basis of experimental facts quantum mechanics have some postulates.

1. **Wave function:** In quantum mechanics, the state of a particle is represented by a wave functionψ. ψ Is also called state function. It may be real or complex. $\psi$is a function of position (space) and time. That is $\psi = \psi(r,t)$or$\psi = \psi(x,y,z,t)$.

For N Particles,

$$\psi = \psi(r_1, r_2, - - -, t)$$

$$\psi = \psi(x_1, y_1, z_1, x_2, y_2, z_2, - - -, t)$$

Density of the states or probability of the states is represented by p.

Where$P = \psi^*\psi = |\psi|^2$

Here ψ^* is the complex conjugate ofψ. Here $Pdv = \psi^*\psi dv = |\psi|^2 dv$ is called probability density.

2. Operator: In classical mechanics a physical quantity such as position, momentum, energy and angular momentum etc. can be determined experimentally is called observable quantity or dynamical variable. In quantum mechanics, these observable quantities are named as **operator**. In generally an operator is represented by$\hat{A}$.

For example

a) Position operator $\hat{r}$
b) Momentum operator $\hat{p}$
c) Kinetic energy operator $\hat{T}$
d) Total energy operator $\hat{H}$
e) Angular momentum operator $\hat{L}$

When an operator acts upon a wave function, some constant value related to operator is obtained. For example when energy operator acts on a wave function then corresponding value in the unit of joule or electron volt will be obtained.

Operator acts on a wave function such that a new wave function reproduce with some constant value related to that operator. For example

$$\hat{A}\psi = a\phi$$

3. **Eigen function and Eigen value:** If an operator acts on a wave function such that the same wave function reproduce with some constant value related to that operator then that wave function is called Eigen function and the cross ponding constant value is called Eigen value.

For example

$$\hat{A}\psi = a\psi$$

Here $\hat{A}$ is an operator that acted upon a wave function $\boldsymbol{\psi}$**.**As a result of that same wave function is reproduced with some constant value a. So here $\boldsymbol{\psi}$ is an Eigen function and $\boldsymbol{a}$is an Eigen value which can be real or complex. Schrodinger's equation is an Eigen value equation that is written as

$$\hat{H}\psi = E\psi$$

Here $\hat{H}$ is called Hamiltonian operator or total energy operator.

$$\hat{H} = \hat{T} + \hat{U} = \frac{\hat{P}^2}{2m} + \hat{U}$$

4. Normalization: The total probability of finding the particle somewhere must be unity. For this we require

$$\int_{-\infty}^{+\infty} \psi^* \psi \, dv = 1$$

Here integral extends over all volume in which the particle is confined. The wave function which satisfy the above relation is said to be normalized to unity.

5. Time dependent wave function: The time dependent wave function will be obtained by solving the Schrodinger's time dependent equation.

$$\hat{H}\psi = -i\hbar \frac{\delta\psi}{\delta t}$$

Here $\psi = \psi(r, t)$

6. Time independent wave function: The time independent wave function will be obtained by solving the Schrodinger's time independent equation.

$$\hat{H}\psi = E\psi$$

Here $\psi = \psi(r)$

7. Expectation or average value of an operator: if an operator $\hat{A}$ acts upon a wave function ψThe expectation value of $\hat{A}$ is written as $< \hat{A} >$

$$\text{Here} < \hat{A} > = \frac{\int_{-\infty}^{+\infty} \psi^* \hat{A} \psi dv}{\int_{-\infty}^{+\infty} \psi^* \psi dv}$$

For normalized condition

$$\int_{-\infty}^{+\infty} \psi^* \psi \, dv = 1$$

$$\text{So} < \hat{A} > = \int_{-\infty}^{+\infty} \psi^* \hat{A} \psi \, dv$$

Values of different quantum mechanical operators

1. Nabla operator: It is differential operator, represented by ∇.

$$\nabla = \frac{\partial}{\partial \mathrm{x}} \hat{\imath} + \frac{\partial}{\partial \mathrm{y}} \hat{\jmath} + \frac{\partial}{\partial \mathrm{z}} \hat{k}$$

2. Laplacian operator: It is second order differential operator. It is represented by∇^2.

$$\nabla^2 = \frac{\partial^2}{\partial \mathrm{x}^2} + \frac{\partial^2}{\partial \mathrm{y}^2} + \frac{\partial^2}{\partial \mathrm{z}^2}$$

3. Linear momentum operator: It is represented by $\hat{P}$.

$$\hat{P} = -i\hbar\nabla$$

$$\hat{P} = -i\hbar\left(\frac{\partial}{\partial \mathrm{x}} \hat{\imath} + \frac{\partial}{\partial \mathrm{y}} \hat{\jmath} + \frac{\partial}{\partial \mathrm{z}} \hat{k}\right)$$

$$\hat{P_x} = -i\hbar \frac{\partial}{\partial \mathrm{x}} \, , \hat{P_y} = -i\hbar \frac{\partial}{\partial \mathrm{y}} \, , \hat{P_z} = -i\hbar \frac{\partial}{\partial \mathrm{z}}$$

4. Angular momentum operator: It is represented by $\hat{L}$.

$$\hat{L} = \hat{r} \times \hat{P} == -i\hbar \hat{r} \times \nabla$$

5. Kinetic energy operator: It is represented by $\hat{K}$.

$$\hat{K} = \frac{P^2}{2m} = \frac{-\hbar^2 \nabla^2}{2m}$$

6. Total energy operator: it is represented by $\hat{E}$.

$$\hat{E} = i\hbar\frac{\partial}{\partial t}$$

7. Hamiltonian operator: It is another total energy operator. It is represented by$\hat{H}$.

$$\hat{H} = K.E + P.E = \hat{K} + \hat{V} = \frac{-\hbar^2\nabla^2}{2m} + \hat{V}$$

8. D,Almbert operator: It is represented by $\square^2$.

$$\square^2 = \nabla^2 \ -\frac{1}{C^2}\frac{\partial^2}{\partial t^2}$$

Adjoint of an operator: Let $\hat{A}$ is an operator then adjoint of this operator is written as $\overset{\dagger}{A}$

Here the symbol † is called dagger. $\overset{\dagger}{A}$ Means Hermitian conjugate of$\hat{A}$ .In quantum mechanics almost all the operators are Hermitian. Now $\hat{A}$ is related to $\overset{\dagger}{A}$ by the relation

$$\int_{-\infty}^{+\infty} \left(\hat{A}\psi\right)^* \Phi dv = \int_{-\infty}^{+\infty} \psi^* \overset{\dagger}{A}\Phi dv$$

If $\hat{A}$ is hermitian operator then $\overset{\dagger}{A} = \hat{A}$

Properties of Eigen Functions

1. Orthonormal Eigen Functions: If ψ_m and ψ_n two orthonormal Eigen functions then quantum mechanically orthonormality condition is written as

$$\int_{-\infty}^{+\infty} {\psi_m}^* \ \psi_n dv = \delta_{mn}$$

δ_{mn} is called kronecker delta. Where $\delta_{mn} = \begin{cases} 0 & if\ m \neq n \\ 1 & if\ m = n \end{cases}$

2. Complete set of Eigen functions: let we have a set of Eigen functions $\psi_1, \psi_2, --, \psi_n$ then their linear combination will be

$$a_1\psi_1 + a_2\psi_2 + - - + a_n\psi_n = \sum_{i=1}^{i=n} a_i\psi_i$$

If these wave functions converge and define a new wave function such that

$$\psi = \sum_{i=1}^{i=n} a_i\psi_i$$

Then Eigen functions are called a complete set of Eigen functions.

3. De-generate Eigen functions: Different Eigen functions having same Eigen values are called De-generate Eigen functions. Let ψ_m and ψ_n two Eigen functions and

$$\hat{A}\psi_m = a\psi_m$$
$$\hat{A}\psi_n = a\psi_n$$

In above case Eigen value of both wave function is a. So ψ_m and ψ_n are Degenerate Eigen functions.

4. Linearly independent Eigen functions: let we have a set of Eigen functions $\psi_1, \psi_2, --, \psi_n$ then their linear combination will be

$$a_1\psi_1 + a_2\psi_2 + - - + a_n\psi_n = \sum_{i=1}^{i=n} a_i\psi_i$$

If $\sum_{i=1}^{i=n} a_i\psi_i = 0$

Such that

$$\sum_{i=1}^{i=n} a_i = 0 \quad that\ is\ \ a_1 = a_2 = - - - = a_n = 0$$

Then Eigen functions are called linearly independent.

5. Simultaneous Eigen function: if Different operator acts on a same wave function then wave function is called simultaneous wave function of those operators.

$$\hat{A}\psi_m = a\psi_m$$
$$\hat{B}\psi_m = b\psi_m$$

Here $\psi_m$is the simultaneous Eigen function of the operators $\hat{A}$ and $\hat{B}$ with Eigen values *a* and *b*. Operators $\hat{A}$ and $\hat{B}$ here are called compatible operators.

CHAPTER 4
MATRIX FORMULATION

Ket-Bra notation

According to Dirac, in Newtonian mechanics a vector is represented by $\vec{A}$.In space it is written as $\vec{A} = A_x\hat{\imath} + A_y\hat{\jmath} + A_z\hat{k}$

Here $\hat{\imath}.\hat{\jmath} and \hat{k}$ are called unit vectors or basis vectors. Now $\vec{A}$ can be written as

$$\vec{A} = A_x\begin{pmatrix}1\\0\\0\end{pmatrix} + A_y\begin{pmatrix}0\\1\\0\end{pmatrix} + A_z\begin{pmatrix}0\\0\\1\end{pmatrix}$$

$$\vec{A} = \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix}$$

$$\vec{A} = /\vec{A} >$$

This vertical line / and angular bracket > is collectively called Ket />. So ket vector is a column vector. If we take a complex conjugate of Ket, we get Bra <\.Here Bra is a row vector. That is $\left(/\vec{A} >\right)^* = < \vec{A}\backslash$

Here the symbol * means complex conjugate.

As $$/\vec{A} >= \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix}$$

So $$< \vec{A}\backslash = /\vec{A} >^* = \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix}^* = (A_x \quad A_y \quad A_z)$$

Dirac said that in quantum Mechanics, wave function ψ is also a vector called state vector. It can be represented in n dimensional space called configuration space or Hilbert space.

So, ψ can be written in the form of Ket and Bra notations. So $\psi\ ket$ will be

$$/\psi >= \begin{pmatrix} A_1 \\ A_2 \\ \vdots \end{pmatrix}$$

$$< \psi\backslash = (A_1 \quad A_2 \quad \cdots)$$

Properties of Ket and Bra

1. If $\hat{A}$ is an operator that acts on a ket $/\psi >$ then quantum mechanically according with Ket Bra notation, it is written as

$$\hat{A}/\psi > = a/\psi >$$

Here *a* is Eigen value of the operator$\hat{A}$.

2. If $\hat{A}$ acts on a Bra$< \psi /$ then it is written as

$$< \psi/\hat{A} = a^* < \psi/$$

Here a^* is a complex Eigen value.

3. Inner product or scalar product: Multiplication of Ket with a Bra such that it gives some number then it is called inner product.

Let$/\psi_n >$ is a Ket vector and $< \psi_m/$ is a Bra vector.Then their inner product is written as

$$< \psi_m//\psi_n > =< \psi_m/\psi_n >= \ number$$

4. Outer product or cross product: Multiplication of Ket with a Bra such that it gives some operator then it is called outer product.

Let$/\psi_n >$ is a Ket vector and $< \psi_m/$ is a Bra vector.Then their outer product is written as

$$/\psi_n >< \psi_m/ = operator$$

5. **Integration:** Integration of the state vectors $\psi_n$and ψ_m over the given volume in quantum mechanics is written as

$$\int_{-\infty}^{+\infty} \psi_m \psi_n dv$$

In Ket Bra notation it is written as

$$\int_{-\infty}^{+\infty} \psi_m \psi_n dv =< \psi_m/\psi_n >$$

6. Normalization: Normalization condition is written as

$$< \psi_m/\psi_n >= \delta_{mn}$$

If $m = n$ **then** $\delta_{mn} = 1$

$$< \psi_m/\psi_n >= 1$$

If $m \neq n$ then$\delta_{mn} = 0$

$$< \psi_m/\psi_n >= 0$$

7. Distributive property:

$$< \psi/(a_1/\psi_1 > + a_2/\psi_2 >)$$
$$< \psi/a_1/\psi_1 > + < \psi/a_2/\psi_2 >$$
$$a_1 < \psi/\psi_1 > + a_2 < \psi/\psi_2 >$$

Here$a_1 \ and \ a_2$ are any numbers.

8. Expectation value of an operator

Quantum mechanically expectation value of an operator is written as

$$< \hat{A} >= \frac{\int_{-\infty}^{+\infty} \psi^* \hat{A} \psi \, dv}{\int_{-\infty}^{+\infty} \psi^* \psi \, dv}$$

In ket bra notation it is written as

$$< \hat{A} >= \frac{< \psi^* / \hat{A} / \psi >}{< \psi^* / \psi >}$$

The expectation value of an operator is equal to Eigen value .If we have many wave functions then it will be equal to weighed sum of all the Eigen values. Let we have an Eigen value equation

$$\hat{A} / \psi >= a / \psi >$$

Now

$$< \hat{A} >= \frac{< \psi^* / \hat{A} / \psi >}{< \psi^* / \psi >}$$

$$< \hat{A} >= \frac{\int_{-\infty}^{+\infty} \psi^* \hat{A} \psi \, dv}{\int_{-\infty}^{+\infty} \psi^* \psi \, dv} = \frac{a \int_{-\infty}^{+\infty} \psi^* \psi \, dv}{\int_{-\infty}^{+\infty} \psi^* \psi \, dv} = a$$

For complete set of wave functions

$$/ \psi >= \sum c_i / \psi_i >$$

Now

$$< \hat{A} >= \frac{\int_{-\infty}^{+\infty} \psi^* \hat{A} \psi \, dv}{\int_{-\infty}^{+\infty} \psi^* \psi \, dv} = \frac{a \sum {c_i}^* c_i \int_{-\infty}^{+\infty} \psi^* \psi \, dv}{\int_{-\infty}^{+\infty} \psi^* \psi \, dv} = a \sum |c_i|^2$$

Quantum mechanical Operator and its properties in Ket Bra notation

Operator: In classical mechanics a physical quantity such as position, momentum, energy and angular momentum etc. can be determined experimentally is called observable

quantity or dynamical variable. In quantum mechanics, these observable quantities are named as **operator**. In generally an operator is represented by$\hat{A}$.

For example

a) Position operator $\hat{r}$

b) Momentum operator $\hat{p}$

c) Kinetic energy operator $\hat{T}$

d) Total energy operator $\hat{H}$

e) Angular momentum operator $\hat{L}$

When an operator acts upon a wave function, some constant value related to operator is obtained. For example when energy operator acts on a wave function then corresponding value in the unit of joule or electron volt will be obtained.

Operator acts on a wave function such that a new wave function reproduces with some constant value related to that operator. For example

$$\hat{A}/\psi >= a/\phi >$$

Properties

Some important properties of operator are

1. **Addition:** Let we have two operators $\hat{A}$and $\hat{B}$acts on a wave function $/\psi >$.Then

$$\left[\hat{A} + \hat{B}\right]/\psi >= \hat{A}/\psi > +\hat{B}/\psi >$$

2. **Subtraction:** Let we have two operators $\hat{A}$and $\hat{B}$acts on a wave function $/\psi >$.Then

$$\left[\hat{A} - \hat{B}\right]/\psi >= \hat{A}/\psi > -\hat{B}/>$$

3. **Product:** Let we have two operators $\hat{A}$and $\hat{B}$acts on a wave function $/\psi >$.Then

$$(\hat{A}\hat{B})/\psi >= \hat{A}\,(\hat{B}/\psi >)$$

4. **Linearity:** Let$/\psi_1 >$and $/\psi_2 >$ are the state vectors of the operator $\hat{A}$

Then according to the linearity

$$\hat{A}(/\psi_1 > +/\psi_2 >) = \hat{A}/\psi_1 > +\hat{A}/\psi_2 >$$

5. **Associative property:** let $\hat{A}, \hat{B}\ and\ \hat{C}$ are the operators of a wave function $/\psi >$then

$$(\widehat{A}\,\hat{B}\hat{C})/\psi >= (\widehat{A\,B})\hat{C}/\psi >$$

6. **Exponent form of an operator:** if $\widehat{A}$ is an operator and it is in exponent such that $e^{\widehat{A}}$

$$\text{then } e^{\widehat{A}} = 1 + \widehat{A} + \frac{\widehat{A}^2}{2!} + \frac{\widehat{A}^3}{3!} + \ - - -$$

7. Matrix form an operator: An operator can be written in matrix form to map one basis vector to another.let $\widehat{A}$ is an operator then matrix form of $\widehat{A}$ is written as

$$\widehat{A} = < \psi_m / \widehat{A} / \psi_n > = \widehat{A}_{mn}$$

$$\widehat{A} = \begin{vmatrix} A_{11} & A_{12} & \dots & A_{1n} \\ A_{21} & A_{22} & \dots & A_{2n} \\ \vdots & \vdots & \dots & \vdots \\ A_{n1} & A_{n2} & \dots & A_{nn} \end{vmatrix}$$

8. **Hermitian operator:** An operator $\widehat{A}$ is called Hermitian if

$$\overset{\dagger}{A} = \widehat{A}$$

Here the symbol $\dagger$ is called dagger. $\overset{\dagger}{A}$ means Hermitian conjugate of$\widehat{A}$ .In quantum mechanics almost all the operators are Hermitian. Properties of Hermitian operators are

a. Sum of two Hermitian operators is Hermitian
b. Product of two commuting Hermitian operators is Hermitian.
c. Eigen value of Hermitian operator is real.
d. Two eigen functions of a Hermitian operator are orthogonal.
e. If ψ_1 and ψ_2 are two linearly independent wave functions of the same operator $\widehat{A}$ belonging to same Eigen values then any linear combination of ψ_1 and ψ_2 will be Eigen function with same Eigen value.
f. Total probability density of a wave function will constant if and only if Hamiltonian of the system is Hermitian.
g. An Eigen value of two anti- Hermitian operators is imaginary or zero.
h. If two Hermitian operators commute and have no degenerate Eigen value then each Eigen function of one operator will be the Eigen function of other operator.

9. **Unitary operator:** A unitary operator is represented by $\widehat{U}$ .For unitary operator

$$\overset{\dagger}{U} = \widehat{U}$$

$$\overset{\dagger}{U}\widehat{U}^{-1} = I$$

Here$I$ is identity matrix. In quantum mechanics unitary matrix is used for rotation.

10. Identity matrix: Identity matrix is represented by ***I*** where$I/\psi>=/\psi>$. That is Eigen value of identity matrix is 1.

11. Commutation property: if $\widehat{A}$ and $\widehat{B}$ are two operators then quantum mechanically their commutation relation is written as

$$\left[\widehat{A}, \widehat{B}\right] = \widehat{A}\,\widehat{B} - \widehat{B}\,\widehat{A}$$

Here square bracket [ ] is called commutator bracket.

If $\left[\widehat{A}, \widehat{B}\right] = 0$ then $\widehat{A}$ and $\widehat{B}$ are said to commute.

If $\left[\widehat{A}, \widehat{B}\right] \neq 0$ then $\widehat{A}$ and $\widehat{B}$ are said to not commute.

If $\widehat{A}$ and $\widehat{B}$ are commute then it means we can find exact and accurate values. But if $\widehat{A}$ and $\widehat{B}$ are not commute then it means we cannot find exact values but approximate and uncertain values. In quantum physics, generally results are not accurate but uncertain. So quantum mechanically all the operators are almost do not commute.

Ehrenfest's Theorem

This theorem states that time evaluation of Expectation value of a quantum mechanical operator obey the laws of classical mechanics.

We know that Expectation value of an operator $\hat{A}$ is

$$<\hat{A}> = \frac{<\psi^*/\widehat{A}/\psi>}{<\psi^*/\psi>}$$

If wave functions are normalized then

$$<\hat{A}> = <\psi^*/\widehat{A}/\psi> = \int_{-\infty}^{+\infty} \psi^* \hat{A} \psi \, dv$$

Differentiate above equation wrt to t

$$\frac{d<\hat{A}>}{dt} = \int_{-\infty}^{+\infty} \frac{\partial}{\partial t}\left(\psi^* \hat{A}\psi\right) dv$$

$$\frac{d<\hat{A}>}{dt} = \int_{-\infty}^{+\infty} \left(\frac{\partial\psi^*}{\partial t}\hat{A}\psi + \psi^* \frac{\partial\psi}{\partial t}\hat{A} + \psi^* \frac{\partial\hat{A}}{\partial t}\psi\right) dv \text{ ------ (1)}$$

As Schrodinger's equation is

$$i\hbar \frac{\partial\psi}{\partial t} = \hat{H}\psi$$

$$\Rightarrow \frac{\partial\psi}{\partial t} = \frac{\hat{H}}{i\hbar}\psi$$

$$\Rightarrow \frac{\partial\psi^*}{\partial t} = \frac{-\left(\hat{H}\psi\right)^*}{i\hbar}$$

Use these values in equation 1

$$\frac{d<\hat{A}>}{dt} = \int_{-\infty}^{+\infty} \left(\frac{-\left(\hat{H}\psi\right)^*}{i\hbar}\hat{A}\psi + \psi^*\hat{A}\frac{\hat{H}\psi}{i\hbar} + \psi^*\frac{\partial\hat{A}}{\partial t}\psi\right) dv$$

$$\frac{d<\hat{A}>}{dt} = \frac{1}{i\hbar}\int_{-\infty}^{+\infty} \left(-\left(\hat{H}\psi\right)^*\hat{A}\psi + \psi^*\hat{A}\hat{H}\psi\right) dv + \int_{-\infty}^{+\infty} \psi^*\frac{\partial\hat{A}}{\partial t}\psi d$$

$$\frac{d<\hat{A}>}{dt} = \frac{1}{i\hbar}\int_{-\infty}^{+\infty} \left(-\psi^* \overset{\dagger}{H}\hat{A}\psi + \psi^*\hat{A}\hat{H}\psi\right) dv + \int_{-\infty}^{+\infty} \psi^*\frac{\partial\hat{A}}{\partial t}\psi dv$$

As for Hermitian operator $\overset{\dagger}{H} = \hat{H}$

$$\frac{d<\hat{A}>}{dt} = \frac{1}{i\hbar}\int_{-\infty}^{+\infty} \left(-\psi^*\hat{H}\hat{A}\psi + \psi^*\hat{A}\hat{H}\psi\right) dv + \int_{-\infty}^{+\infty} \psi^*\frac{\partial\hat{A}}{\partial t}\psi dv$$

$$\frac{d<\hat{A}>}{dt} = \frac{1}{i\hbar}\int_{-\infty}^{+\infty} \left(-\psi^*\hat{H}\hat{A}\psi + \psi^*\hat{A}\hat{H}\psi\right) dv + \int_{-\infty}^{+\infty} \psi^*\frac{\partial\hat{A}}{\partial t}\psi dv$$

$$\frac{d<\hat{A}>}{dt} = \frac{1}{i\hbar}\int_{-\infty}^{+\infty}\left(\psi^*\left(\hat{A}\hat{H}-\hat{H}\hat{A}\right)\psi\right)dv + \int_{-\infty}^{+\infty}\psi^*\frac{\partial\hat{A}}{\partial t}\psi dv$$

$$\frac{d<\hat{x}>}{dt} = \langle\frac{1}{i\hbar}\left[\hat{x},\hat{H}\right]\rangle + \langle\frac{\partial\hat{x}}{\partial t}\rangle$$

This is Eherenfest's equation. This is also called equation of motion or motion integral.

If $\hat{A}$ does not depends explicitly on time then $\langle\frac{\partial\hat{A}}{\partial t}\rangle = 0$. More if $\hat{A}$ and $\hat{H}$ commute then$\left[\hat{A},\hat{H}\right] = 0$ hence $\frac{d<\hat{A}>}{dt} = 0$ which means operator is constant in time or operator is constant of motion.

Now we apply this theorem and verify that time evaluation of expectation value of an operator gives classical mechanics results.

a. Time evaluation of Position operator $\hat{x}$

   As Ehrenfest's theorem is

$$\frac{d<\hat{A}>}{dt} = \langle\frac{1}{i\hbar}\left[\hat{A},\hat{H}\right]\rangle + \langle\frac{\partial\hat{A}}{\partial t}\rangle$$

$$\frac{d<\hat{x}>}{dt} = \langle\frac{1}{i\hbar}\left[\hat{x},\hat{H}\right]\rangle + \langle\frac{\partial\hat{x}}{\partial t}\rangle$$

We replaced $\hat{A}$ with $\hat{x}$. Now $\langle\frac{\partial\hat{x}}{\partial t}\rangle = 0$ because $\hat{x}$ does not explicitly depends on t.

$$\Rightarrow \frac{d<\hat{x}>}{dt} = \langle\frac{1}{i\hbar}\left[\hat{x},\hat{H}\right]\rangle$$

$$\Rightarrow \frac{d<\hat{x}>}{dt} = \langle\frac{1}{i\hbar}\left[\hat{x},\frac{P^2}{2m}+V\right]\rangle$$

$$\frac{d<\hat{x}>}{dt} = \frac{1}{i\hbar}\langle\left[\hat{x},\frac{P^2}{2m}\right]+[\hat{x},V]\rangle$$

As $[\hat{x},V] = 0$ and $\left[\hat{x},\frac{P^2}{2m}\right] = \frac{1}{2m}\left\{\hat{P}\left[\hat{x},\hat{P}\right]+\left[\hat{x},\hat{P}\right]\hat{P}\right\} = \frac{1}{2m}\left(i\hbar\hat{P}+i\hbar\hat{P}\right) = \frac{i\hbar\hat{P}}{m}$

so above equation will become

$$\frac{d<\hat{x}>}{dt} = \frac{1}{i\hbar}\langle\frac{i\hbar\hat{P}}{m}\rangle = \frac{\hat{P}}{m}$$

$$m\,v = \hat{P}$$

This is classical momentum formula.

b. Time evaluation of momentum operator $\hat{P}$

As Ehrenfest's theorem is

$$\frac{d<\hat{A}>}{dt} = \langle\frac{1}{i\hbar}\left[\hat{A},\hat{H}\right]\rangle + \langle\frac{\partial\hat{A}}{\partial t}\rangle$$

$$\frac{d<\hat{P}>}{dt} = \langle\frac{1}{i\hbar}\left[\hat{P},\hat{H}\right]\rangle + \langle\frac{\partial\hat{P}}{\partial t}\rangle$$

We replaced $\hat{A}$ with $\hat{P}$. Now $\langle\frac{\partial\hat{P}}{\partial t}\rangle = 0$ because $\hat{P}$ does not explicitly depends on t.

$$\Rightarrow \frac{d<\hat{P}>}{dt} = \langle\frac{1}{i\hbar}\left[\hat{P},\hat{H}\right]\rangle$$

$$\Rightarrow \frac{d<\hat{P}>}{dt} = \langle\frac{1}{i\hbar}\left[\hat{P},\frac{P^2}{2m}+V\right]\rangle$$

$$\frac{d<\hat{P}>}{dt} = \frac{1}{i\hbar}\langle\left[\hat{P},\frac{P^2}{2m}\right]+\left[\hat{P},V\right]\rangle$$

As $\left[\hat{P},\frac{P^2}{2m}\right]=0$ and $\left[\hat{P},V\right]=\hat{P}V-V\hat{P}$ multiply by orbitrary wave function ψ

$$\left[\hat{P},V\right]\psi = \hat{P}V\psi - V\hat{P}\psi$$

$$\left[\hat{P},V\right]\psi = -i\hbar\frac{\partial}{\partial x}(V\psi) - V\left(-i\hbar\frac{\partial}{\partial x}\right)\psi$$

$$\left[\hat{P},V\right]\psi = -i\hbar\psi\frac{\partial V}{\partial x} - i\hbar V\frac{\partial\psi}{\partial x} + i\hbar V\frac{\partial\psi}{\partial x}$$

$$\left[\hat{P},V\right] = -i\hbar\frac{\partial V}{\partial x}$$

Use this value in above equation

$$\frac{d<\hat{P}>}{dt} = \frac{1}{i\hbar}\langle -i\hbar\frac{\partial V}{\partial x}\rangle$$

$$\frac{d<\hat{P}>}{dt} = \langle -\frac{\partial V}{\partial x} \rangle = -\nabla V = F$$

$$\frac{d<\hat{P}>}{dt} = F$$

This is classical Newton's second law equation.

Correspondence Principle

Bohr atomic model gives discrete energy levels and discrete spectrum but classically atom gives continuous spectrum. Bohr confused to see these different results at quantum level and classical level. He resolved this issue by giving correspondence principle. This principle states that "Quantum theory must agree with classical theory in the limit of large quantum number." This theory also explained as classical theory is a limiting case of quantum theory in the limit in which Plank's constant $h \to 0$.

For example classical simple pendulum vibrates with a specific energy, when air resistance acts on it its amplitude starts to decreases continuously but not in jumps or quanta. Since, in this case planks constant h is so small that jumps may be there but too small to detect. Hence we cannot dismissal the quantization of energy there. In fact, in this case classical theory works well, so there is no need to apply quantum theory. Similarly quantum mechanical Schrodinger's equation for large quantum number gives the result as Newton's second law.

Complementary principle

We know that electromagnetic waves have dual nature wave as well as particle. Complementary principle states that" for complete description both wave and particle natures of a quantum mechanical entity are compulsory, but these two aspects cannot occur simultaneously in a single experiment."

For example when we do experiment of diffraction or polarization, electromagnetic wave shows wave nature but not particle nature. Similarly when we do photoelectric effect

experiment, electromagnetic wave shows particle nature stream of photons but does not show wave nature.

Some important theorem about operators

Theorem1

Statement: Eigen values of Hermitian operators are real.

Proof: Consider a Hermitian operator $\hat{A}$ acts on a wave function $/\psi >$ so quantum mechanically we can write

$$\hat{A}\,/\psi >= a/\psi > \text{--------1}$$

Here a is the Eigen value of operator$\hat{A}$. We take the complex conjugate of equation 1.

$$\left(\hat{A}\,/\psi >\right)^{*} = (a/\psi >)^{*}$$

$$< \psi/\overset{\dagger}{A} = a^{*} < \psi/ \text{-------2}$$

Multiply equation 1 with $< \psi/$ and equation 2 with $/\psi >$, we get

$$< \psi/\hat{A}\,/\psi >=< \psi/a/\psi >$$

$$< \psi/\hat{A}\,/\psi >= a < \psi/>$$

But according to normalized condition$< \psi/\psi >= 1$ so above equation will become

$$< \psi/\hat{A}\,/\psi >= a \text{ ---------3}$$

Similarly equation 2

$$< \psi/\overset{\dagger}{A}/\psi >= a^{*} < \psi//\psi >$$

But according to normalized condition$< \psi/\psi >= 1$ so above equation will become

$$< \psi/\overset{\dagger}{A}/\psi >= a^{*} \text{ ----------4}$$

According to definition of Hermitian operator

$$\overset{\dagger}{A} = \widehat{A}$$

So equation 4 will become

$$< \psi/\widehat{A}\,/\psi >= a^{*} \text{ ----------5}$$

Now compering equations 3 and 5 we get

$$a^{*} = a$$

This relation shows that Eigen values of Hermitian operator are real.

Theorem2

Statement: Eigen values of different wave functions are orthogonal.

Proof: Consider a Hermitian operator $\widehat{A}$ acts on two different wave functions $/\psi_m >$ and $/\psi_n >$ .Here $m \neq n$.

Now quantum mechanically we can write

$$\widehat{A}\,/\psi_m >= a_m/\psi_m > \text{ --------1}$$

Here a_m is the Eigen value of operator$\widehat{A}$. Similarly

$$\widehat{A}\,/\psi_n >= a_n/\psi_n > \text{ --------2}$$

Here a_n is the Eigen value of operator$\widehat{A}$

We take the complex conjugate of equations 1 and 2.

$$\left(\widehat{A}\,/\psi_m >\right)^{*} = (a_m/\psi_m >)^{*}$$

$$< \psi_m/\overset{\dagger}{A} = {a_m}^{*} < \psi_m/ \text{ -------3}$$

Similarly $$< \psi_n/\overset{\dagger}{A} = {a_n}^{*} < \psi_n/ \text{ -------4}$$

Multiply equation 3 with $/\psi_n >$ and equation 2 with $/\psi_m >$, we get

$$< \psi_m/\overset{\dagger}{A}/\psi_n >= {a_m}^{*} < \psi_m/\psi_n > \text{ -------5}$$

$$< \psi_n / \overset{\dagger}{A} / \psi_m >= a_n{}^* < \psi_n / \psi_m > \text{ -------6}$$

As $\widehat{A}$ is Hermitian operator so

$$\overset{\dagger}{A} = \widehat{A}$$

So equations5 and 6 will become

$$< \psi_m / \widehat{A} / \psi_n >= a_m{}^* < \psi_m / \psi_n >$$

$$a_n < \psi_m / \psi_n >= a_m{}^* < \psi_m / \psi_n >$$

$$(a_n - a_m{}^*) < \psi_m / \psi_n >= 0$$

$$(a_n - a_m{}^*)\delta_{mn} = 0$$

If $m = n$**then** $\delta_{mn} = 1$

$$< \psi_m / \psi_n >= 1$$

If $m \neq n$ then$\delta_{mn} = 0$

$$< \psi_m / \psi_n >= 0$$

But in our case $m \neq n$so$\delta_{mn} = 0$

Similarly equation 6 will be

$$< \psi_n / \widehat{A} / \psi_m >= a_n{}^* < \psi_n / \psi_m >$$

$$a_m < \psi_n / \psi_m >= a_n{}^* < \psi_n / \psi_m >$$

$$(a_m - a_n{}^*) < \psi_n / \psi_m >= 0$$

$$(a_m - a_n{}^*)\delta_{mn} = 0$$

If $m = n$ then $\delta_{mn} = 1$

$$< \psi_n / \psi_m >= 1$$

If $m \neq n$ then$\delta_{mn} = 0$

$$< \psi_n / \psi_m >= 0$$

But in our case $m \neq n$so$\delta_{mn} = 0$

The above calculations show that $/\psi_m >$ and $/\psi_n >$ are orthogonal to each other.

Hence Eigen values of different wave functions are orthogonal.

Theorem3

Statement: Commutator of two Hermitian operators is skew Hermitian or anti Hermitian.

Proof: Let we have two Hermitian operators $\hat{A}$ and $\hat{B}$ satisfying the condition

$$\overset{\dagger}{A} = \hat{A}$$

$$\overset{\dagger}{B} = \hat{B}$$

Now commutation relation of $\hat{A}$ and $\hat{B}$ by definition is

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

Taking the complex conjugate on both sides

$$\left[\hat{A}, \hat{B}\right]^{\dagger} = (\hat{A}\hat{B})^{\dagger} - (\hat{B}\hat{A})^{\dagger}$$

But according to definition

$$(\hat{A}\hat{B})^{\dagger} = \hat{B}^{\dagger}\hat{A}^{\dagger} \qquad \text{And} \qquad (\hat{B}\hat{A})^{\dagger} = \hat{A}^{\dagger}\hat{B}^{\dagger}$$

So $$\left[\hat{A}, \hat{B}\right]^{\dagger} = \hat{B}^{\dagger}\hat{A}^{\dagger} - \hat{A}^{\dagger}\hat{B}^{\dagger}$$

$$\left[\hat{A}, \hat{B}\right]^{\dagger} = \hat{B}\hat{A} - \hat{A}\hat{B} \text{ \{By definition\}}$$

$$\left[\hat{A}, \hat{B}\right]^{\dagger} = -(\hat{A}\hat{B} - \hat{B}\hat{A})$$

$$\left[\hat{A}, \hat{B}\right]^{\dagger} = -\left[\hat{A}, \hat{B}\right]$$

This equation shows that Commutator of two Hermitian operators is skew Hermitian or anti Hermitian.

Theorem4

Statement: Sum of two Hermitian operators is Hermitian.

Proof: Let we have two Hermitian operators $\hat{A}$ and $\hat{B}$ satisfying the condition

$$\overset{\dagger}{A} = \hat{A} \text{ And } \overset{\dagger}{B} = \hat{B}$$

Now $$\left(\hat{A} + \hat{B}\right)^{\dagger} = \overset{\dagger}{A} + \overset{\dagger}{B} = \hat{A} + \hat{B}$$

Theorem5

Statement: Product of two commuting Hermitian operators is Hermitian.

Proof: Let we have two Hermitian operators $\hat{A}$ and $\hat{B}$ satisfying the condition

$$\overset{\dagger}{A} = \hat{A} \text{ And } \overset{\dagger}{B} = \hat{B}$$

Now by definition

$$\int_{-\infty}^{+\infty} \phi^* \left(\hat{A}\,\hat{B}\right)^{\dagger} \psi dx = \int_{-\infty}^{+\infty} \left(\hat{A}\,\hat{B}\right)^{*} \phi^* \psi dx$$

$$\int_{-\infty}^{+\infty} \phi^* \left(\hat{A}\,\hat{B}\right)^{\dagger} \psi dx = \int_{-\infty}^{+\infty} \phi^* \left(\overset{\dagger}{B}\overset{\dagger}{A}\right) \psi dx$$

$$\Rightarrow \left(\hat{A}\,\hat{B}\right)^{\dagger} = \left(\overset{\dagger}{B}\overset{\dagger}{A}\right) = \hat{B}\,\hat{A}$$

For two commuting operators

$$\hat{A}\,\hat{B} - \hat{B}\,\hat{A} = 0$$

$$\Rightarrow \hat{A}\,\hat{B} = \hat{B}\,\hat{A}$$

So above equation becomes

$$\left(\hat{A}\,\hat{B}\right)^{\dagger} = \hat{A}\,\hat{B}$$

Hence product of two commuting Hermitian operators is also Hermitian.

Some important commutation relations

1. $\left[\widehat{P}_x, \widehat{x}\right] = -i\hbar$
2. $\left[\widehat{P}_y, \widehat{y}\right] = -i\hbar$
3. $\left[\widehat{P}_z, \widehat{z}\right] = -i\hbar$
4. $[\widehat{p}, \widehat{r}] = -i\hbar$
5. $\left[\widehat{P}_x, \widehat{y}\right] = 0$
6. $\left[\widehat{P}_x, \widehat{z}\right] = 0$
7. $\left[\widehat{P}_y, \widehat{x}\right] = 0$
8. $\left[\widehat{P}_y, \widehat{z}\right] = 0$
9. $\left[\widehat{P}_z, \widehat{x}\right] = 0$
10. $\left[\widehat{P}_z, \widehat{y}\right] = 0$
11. $\left[\widehat{E}, \widehat{t}\right] = i\hbar$

Proof 1. $\left[\widehat{P}_x, \widehat{x}\right]$

According to definition of commutation relation

$$\left[\widehat{P}_x, \widehat{x}\right] = \widehat{P}_x\widehat{x} - \widehat{x}\,\widehat{P}_x$$

Multiply by $/\psi_x >$

$$\left[\widehat{P}_x, \widehat{x}\right]/\psi_x >= (\widehat{P}_x\widehat{x} - \widehat{x}\,\widehat{P}_x)/\psi_x >$$

But $\widehat{P}_x = -i\hbar\frac{\partial}{\partial x}$ so

$$\left[\widehat{P}_x, \widehat{x}\right]/\psi_x >= (-i\hbar\frac{\partial}{\partial x}\ (\widehat{x}/\psi_x >) - \widehat{x}\,(-i\hbar\frac{\partial}{\partial x}/\psi_x >)$$

$$\left[\widehat{P}_x, \widehat{x}\right]/\psi_x >= -i\hbar\{(\frac{\partial}{\partial x}\ (\widehat{x}/\psi_x >) - \widehat{x}\,(\frac{\partial}{\partial x}/\psi_x >)\}$$

$$\left[\widehat{P}_x, \widehat{x}\right]/\psi_x >= -i\hbar\{(\widehat{x}\,\frac{\partial/\psi_x >}{\partial x}\ + /\psi_x > \frac{\partial\widehat{x}}{\partial x}) - \widehat{x}\,(\frac{\partial/\psi_x >}{\partial x})\}$$

$$\left[\widehat{P}_x, \widehat{x}\right]/\psi_x >= -i\hbar\{(\widehat{x}\,\frac{\partial/\psi_x >}{\partial x}\ + /\psi_x >) - \widehat{x}\,(\frac{\partial/\psi_x >}{\partial x})\}$$

$$\left[\widehat{P}_x, \widehat{x}\right]/\psi_x >= -i\hbar(/\psi_x >)$$

Remove $/\psi_x >$

$$\left[\hat{P}_x, \hat{x}\right] = -i\hbar$$

Proof 2. $\left[\hat{P}_y, \hat{y}\right]$

According to definition of commutation relation

$$\left[\hat{P}_y, \hat{y}\right] = \hat{P}_y\hat{y} - \hat{y}\,\hat{P}_y$$

Multiply by$/\psi_y >$

$$\left[\hat{P}_y, \hat{y}\right]/\psi_y >= (\hat{P}_y\hat{y} - \hat{y}\,\hat{P}_y)/\psi_y >$$

But $\hat{P}_y = -i\hbar\frac{\partial}{\partial y}$ so

$$\left[\hat{P}_y, \hat{y}\right]/\psi_y >= (-i\hbar\frac{\partial}{\partial y}\ (\hat{y}/\psi_y >) - \hat{y}\,(-i\hbar\frac{\partial}{\partial y}/\psi_y >)$$

$$\left[\hat{P}_y, \hat{y}\right]/\psi_y >= -i\hbar\{(\frac{\partial}{\partial y}\ (\hat{y}/\psi_y >) - \hat{y}\,(\frac{\partial}{\partial y}/\psi_y >)\}$$

$$\left[\hat{P}_y, \hat{y}\right]/\psi_y >= -i\hbar\{(\hat{y}\,\frac{\partial/\psi_y >}{\partial y}\ + /\psi_y > \frac{\partial\hat{y}}{\partial y}) - \hat{y}\,(\frac{\partial/\psi_y >}{\partial y})\}$$

$$\left[\hat{P}_y, \hat{y}\right]/\psi_y >= -i\hbar\{(\hat{y}\,\frac{\partial/\psi_y >}{\partial y}\ + /\psi_y >) - \hat{y}\,(\frac{\partial/\psi_y >}{\partial y})\}$$

$$\left[\hat{P}_y, \hat{y}\right]/\psi_y >= -i\hbar(/\psi_y >)$$

Remove $/\psi_y >$

$$\left[\hat{P}_y, \hat{y}\right] = -i\hbar$$

Proof 3. $\left[\hat{P}_z, \hat{z}\right]$

According to definition of commutation relation

$$\left[\hat{P}_z, \hat{z}\right] = \hat{P}_z\hat{z} - \hat{z}\,\hat{P}_z$$

Multiply by$/\psi_z >$

$$\left[\hat{P}_z, \hat{z}\right]/\psi_z >= (\hat{P}_z\hat{z} - \hat{z}\,\hat{P}_z)/\psi_z >$$

But $\hat{P}_z = -i\hbar\frac{\partial}{\partial z}$ so

$$\left[\hat{P}_z, \hat{z}\right]/\psi_z >= (-i\hbar\frac{\partial}{\partial z}\ (\hat{z}/\psi_z >) - \hat{z}(-i\hbar\frac{\partial}{\partial z}/\psi_z >)$$

$$\left[\hat{P}_z, \hat{z}\right]/\psi_z >= -i\hbar\{(\frac{\partial}{\partial z}\ (\hat{z}/\psi_z >) - \hat{z}(\frac{\partial}{\partial z}/\psi_z >)\}$$

$$\left[\hat{P}_z, \hat{z}\right]/\psi_z >= -i\hbar\{(\hat{z}\frac{\partial/\psi_z >}{\partial z}\ + /\psi_z > \frac{\partial\hat{z}}{\partial z}) - \hat{z}(\frac{\partial/\psi_z >}{\partial z})\}$$

$$\left[\hat{P}_z, \hat{z}\right]/\psi_z >= -i\hbar\{(\hat{z}\frac{\partial/\psi_z >}{\partial z}\ + /\psi_z >) - \hat{z}(\frac{\partial/\psi_z >}{\partial z})\}$$

$$\left[\hat{P}_z, \hat{z}\right]/\psi_z >= -i\hbar(/\psi_z >)$$

Remove $/\psi_z >$

$$\left[\hat{P}_z, \hat{z}\right] = -i\hbar$$

Proof 4. $\left[\hat{P}, \hat{r}\right]$

According to definition of commutation relation

$$\left[\hat{P}, \hat{r}\right] = \hat{P}\hat{r} - \hat{r}\hat{P}$$

Multiply by $/\psi_r >$

$$\left[\hat{P}, \hat{r}\right]/\psi_r >= (\hat{P}\hat{r} - \hat{r}\hat{P})/\psi_r >$$

But $\hat{P} = -i\hbar\frac{\partial}{\partial r}$ so

$$\left[\hat{P}, \hat{r}\right]/\psi_r >= (-i\hbar\frac{\partial}{\partial r}\ (\hat{r}/\psi_r >) - \hat{r}(-i\hbar\frac{\partial}{\partial r}/\psi_r >)$$

$$\left[\hat{P}, \hat{r}\right]/\psi_r >= -i\hbar\{(\frac{\partial}{\partial r}\ (\hat{r}/\psi_r >) - \hat{r}(\frac{\partial}{\partial r}/\psi_r >)\}$$

$$\left[\hat{P}, \hat{r}\right]/\psi_r >= -i\hbar\{(\hat{r}\frac{\partial/\psi_r >}{\partial r}\ + /\psi_r > \frac{\partial\hat{r}}{\partial r}) - \hat{r}(\frac{\partial/\psi_r >}{\partial r})\}$$

$$\left[\hat{P}, \hat{r}\right]/\psi_r >= -i\hbar\{(\hat{r}\frac{\partial/\psi_r >}{\partial r}\ + /\psi_r >) - \hat{r}(\frac{\partial/\psi_r >}{\partial r})\}$$

$$\left[\hat{P},\hat{r}\right]/\psi_r >= -i\hbar(/\psi_r >)$$

Remove $/\psi_r >$

$$\left[\hat{P},\hat{r}\right] = -i\hbar$$

Proof 5. $\left[\hat{P}_x,\hat{y}\right]$

According to definition of commutation relation

$$\left[\hat{P}_x,\hat{y}\right] = \hat{P}_x\hat{y} - \hat{y}\,\hat{P}_x$$

Multiply by $/\psi_x >$

$$\left[\hat{P}_x,\hat{y}\right]/\psi_x >= (\hat{P}_x\hat{y} - \hat{y}\,\hat{P}_x)/\psi_x >$$

But $\hat{P}_x = -i\hbar\frac{\partial}{\partial x}$ so

$$\left[\hat{P}_x,\hat{y}\right]/\psi_x >= (-i\hbar\frac{\partial}{\partial x}\ (\hat{y}/\psi_x >) - \hat{y}\,(-i\hbar\frac{\partial}{\partial x}/\psi_x >)$$

$$\left[\hat{P}_x,\hat{y}\right]/\psi_x >= -i\hbar\{(\frac{\partial}{\partial x}\ (\hat{y}/\psi_x >) - \hat{y}\,(\frac{\partial}{\partial x}/\psi_x >)\}$$

$$\left[\hat{P}_x,\hat{y}\right]/\psi_x >= -i\hbar\{(\hat{y}\,\frac{\partial/\psi_x >}{\partial x}\ + /\psi_x > \frac{\partial\hat{y}}{\partial x}) - \hat{y}\,(\frac{\partial/\psi_x >}{\partial x})\}$$

$$\left[\hat{P}_x,\hat{y}\right]/\psi_x >= -i\hbar\{(\hat{y}\,\frac{\partial/\psi_x >}{\partial x}\ + 0) - \hat{y}\,(\frac{\partial/\psi_x >}{\partial x})\}$$

$$\left[\hat{P}_x,\hat{x}\right]/\psi_x >= -i\hbar(0)$$

Remove $/\psi_x >$

$$\left[\hat{P}_x,\hat{x}\right] = 0$$

Similarly

$$\left[\hat{P}_x,\hat{z}\right] = 0\ ,\left[\hat{P}_y,\hat{x}\right] = 0\ ,\left[\hat{P}_y,\hat{z}\right] = 0\ ,\left[\hat{P}_z,\hat{x}\right] = 0\ ,\left[\hat{P}_z,\hat{y}\right] = 0$$

Proof 4. $\left[\hat{E},\hat{t}\right]$

According to definition of commutation relation

$$\left[\hat{E},\hat{t}\right] = \hat{E}\hat{t} - \hat{t}\,\hat{E}$$

Multiply by$/\psi_t >$

$$[\hat{E},\hat{t}]/\psi_t >= (\hat{E}\hat{t} - \hat{t}\hat{E})/\psi_t >$$

But $\hat{E} = i\hbar\frac{\partial}{\partial t}$

$$[\hat{E},\hat{t}]/\psi_t >= (i\hbar\frac{\partial}{\partial t}\ (\hat{t}/\psi_t >) - \hat{t}\,(i\hbar\frac{\partial}{\partial t}/\psi_t >)$$

$$[\hat{E},\hat{t}]/\psi_t >= (i\hbar\{(\frac{\partial}{\partial t}\ (\hat{t}/\psi_t >) - \hat{t}\,(\frac{\partial}{\partial t}/\psi_t >)\}$$

$$[\hat{E},\hat{t}]/\psi_t >= (i\hbar\{(\hat{t}\,\frac{\partial/\psi_t >}{\partial t}\ + /\psi_t > \frac{\partial\hat{t}}{\partial t}) - \hat{t}\,(\frac{\partial/\psi_t >}{\partial t})\}$$

$$[\hat{E},\hat{t}]/\psi_t >= (i\hbar\{(\hat{t}\,\frac{\partial/\psi_t >}{\partial t}\ + /\psi_t > -\hat{t}\,(\frac{\partial/\psi_t >}{\partial t})\}$$

$$[\hat{E},\hat{t}]/\psi_t >= i\hbar(/\psi_t >)$$

Remove $/\psi_t >$

$$[\hat{E},\hat{t}] = \hbar$$

Sample Problems

1. Consider a quantum mechanical wave function is given by

$$\psi = \frac{\sqrt{3}}{3}\psi_1 + \frac{2}{3}\psi_2 + \frac{\sqrt{2}}{3}\psi_3$$

Where all $\psi_1, \psi_2\ and\ \psi_3$ are orthonormal functions.

a. Show that wave function is normalized?

b. Find the probability of finding the system in each state?

c. What is total probability?

Solution:

a. According to orthonormality condition is written as

$$\int_{-\infty}^{+\infty} {\psi_m}^*\ \psi_n dv = \delta_{mn}$$

δ_{mn} is called kronecker delta. Where $\delta_{mn} = \begin{cases} 0 & if\ m \neq n \\ 1 & if\ m = n \end{cases}$ So

$$\int_{-\infty}^{+\infty}\left(\frac{\sqrt{3}}{3}\times\frac{\sqrt{3}}{3}\,\psi_1{}^{*}\psi_1+\frac{\sqrt{3}}{3}\times\frac{2}{3}\psi_2{}^{*}\psi_1+\frac{\sqrt{3}}{3}\times\frac{\sqrt{2}}{3}\psi_3{}^{*}\psi_1+\frac{\sqrt{3}}{3}\times\frac{2}{3}\,\psi_1{}^{*}\psi_2+\frac{2}{3}\times\frac{2}{3}\psi_2{}^{*}\psi_2+\frac{\sqrt{3}}{3}\right.$$
$$\left.\times\frac{2}{3}\psi_3{}^{*}\psi_2+\frac{\sqrt{3}}{3}\times\frac{\sqrt{2}}{3}\,\psi_1{}^{*}\psi_3+\frac{2}{3}\times\frac{\sqrt{2}}{3}\psi_2{}^{*}\psi_3+\frac{\sqrt{2}}{3}\times\frac{\sqrt{2}}{3}\psi_3{}^{*}\psi_3\right)dx$$
$$=\frac{1}{3}+0+0+0+\frac{4}{9}+0+0+0+\frac{2}{9}=1$$

Hence wave function is normalized.

b. Now the probability of ψ_1

$$P=\left|\int_{-\infty}^{+\infty}\psi_1{}^{*}\psi dx\right|^2$$

$$P=\left|\int_{-\infty}^{+\infty}\psi_1{}^{*}\left(\frac{\sqrt{3}}{3}\psi_1+\frac{2}{3}\psi_2+\frac{\sqrt{2}}{3}\psi_3\right)dx\right|^2$$

$$P=\left|\int_{-\infty}^{+\infty}\left(\frac{\sqrt{3}}{3}\psi_1{}^{*}\psi_1+\frac{2}{3}\psi_1{}^{*}\psi_2+\frac{\sqrt{2}}{3}\psi_1{}^{*}\psi_3\right)dx\right|^2$$

$$P=\left|\frac{\sqrt{3}}{3}\right|^2=\frac{3}{9}=\frac{1}{3}$$

Now the probability of ψ_2

$$P=\left|\int_{-\infty}^{+\infty}\left(\frac{\sqrt{3}}{3}\psi_2{}^{*}\psi_1+\frac{2}{3}\psi_2{}^{*}\psi_2+\frac{\sqrt{2}}{3}\psi_2{}^{*}\psi_3\right)dx\right|^2$$

$$P=\left|\frac{2}{3}\right|^2=\frac{4}{9}$$

Now the probability of ψ_3

$$P=\left|\int_{-\infty}^{+\infty}\left(\frac{\sqrt{3}}{3}\psi_3{}^{*}\psi_1+\frac{2}{3}\psi_3{}^{*}\psi_2+\frac{\sqrt{2}}{3}\psi_3{}^{*}\psi_3\right)dx\right|^2$$

$$P=\left|\frac{\sqrt{2}}{3}\right|^2=\frac{2}{9}$$

c. Total probability

$$P = \frac{1}{3} + \frac{4}{9} + \frac{2}{9} = 1$$

2. Which of the following wave functions are acceptable and why?

   a. $\psi = \frac{1}{\sqrt{3}}\psi_1 + \frac{2}{3}\psi_2 + \frac{i}{\sqrt{3}}\psi_3$

   b. $\psi = \frac{1}{\sqrt{3}}\psi_1 + \frac{1}{2}\psi_2 + \frac{1}{6}\psi_3 + \frac{i}{3}\psi_3$

   c. $\psi = \frac{1}{\sqrt{6}}\psi_1 + \frac{2}{3}\psi_2 + \sqrt{\frac{5}{2}}\frac{i}{\sqrt{3}}\psi_3$

   d. $\psi = \frac{i}{\sqrt{2}}\psi_1 + \frac{1}{2}\psi_2 + \frac{1}{\sqrt{5}}\psi_3 + \frac{1}{2\sqrt{5}}\psi_3$

   Solution

   a. $\psi = \frac{1}{\sqrt{3}}\psi_1 + \frac{2}{3}\psi_2 + \frac{i}{\sqrt{3}}\psi_3$

A wave function and its derivative are acceptable if it is finite, single valued, continuous and integrable. Know we check this wave function.

Normality condition is written as

$$\int_{-\infty}^{+\infty} \psi^*\psi \; dv = 1$$

$$\int_{-\infty}^{+\infty} \psi^*\psi \; dv = \int_{-\infty}^{+\infty} \left(\frac{1}{\sqrt{3}}\psi_1 + \frac{2}{3}\psi_2 + \frac{i}{\sqrt{3}}\psi_3\right)^* \left(\frac{1}{\sqrt{3}}\psi_1 + \frac{2}{3}\psi_2 + \frac{i}{\sqrt{3}}\psi_3\right) dv$$

$$\int_{-\infty}^{+\infty} \psi^*\psi \; dv = \int_{-\infty}^{+\infty} \left(\frac{1}{\sqrt{3}}{\psi_1}^* + \frac{2}{3}{\psi_2}^* - \frac{i}{\sqrt{3}}{\psi_3}^*\right)\left(\frac{1}{\sqrt{3}}\psi_1 + \frac{2}{3}\psi_2 + \frac{i}{\sqrt{3}}\psi_3\right) dv$$

$$\int_{-\infty}^{+\infty} \psi^*\psi \; dv = \int_{-\infty}^{+\infty} \left(\frac{1}{\sqrt{3}}{\psi_1}^* \times \frac{1}{\sqrt{3}}\psi_1 + \frac{2}{3}{\psi_2}^* \times \frac{1}{\sqrt{3}}\psi_1 - \frac{i}{\sqrt{3}}{\psi_3}^* \times \frac{1}{\sqrt{3}}\psi_1 + \frac{1}{\sqrt{3}}{\psi_1}^* \times \frac{2}{3}\psi_2 + \frac{2}{3}{\psi_2}^* \times \frac{2}{3}\psi_2 \right.$$
$$\left. - \frac{i}{\sqrt{3}}{\psi_3}^* \times \frac{2}{3}\psi_2 + \frac{1}{\sqrt{3}}{\psi_1}^* \times \frac{i}{\sqrt{3}}\psi_3 + \frac{2}{3}{\psi_2}^* \times \frac{i}{\sqrt{3}}\psi_3 - \frac{i}{\sqrt{3}}{\psi_3}^* \times \frac{i}{\sqrt{3}}\psi_3\right) dv$$

$$\int_{-\infty}^{+\infty} \psi^*\psi \; dv = \int_{-\infty}^{+\infty} \left(\frac{1}{3}{\psi_1}^*\psi_1 + 0 - 0 + 0 + \frac{4}{9}{\psi_2}^*\psi_2 - 0 + 0 + 0 + \frac{1}{3}{\psi_3}^*\psi_3\right) dv$$

$$\int_{-\infty}^{+\infty} \psi^*\psi \; dv = \left(\frac{1}{3} + \frac{4}{9} + \frac{1}{3}\right) = \frac{10}{9} \neq 1$$

So this wave function is not normalized to unity. Hence it is not an acceptable wave function.

Do, part b,c and d in this way.

3. Consider a system whose state is given in term of complete and orthonormal vectors as

$$\psi = \frac{1}{\sqrt{19}}\psi_1 + \frac{2}{\sqrt{19}}\psi_2 + \sqrt{\frac{2}{19}}\psi_3 + \sqrt{\frac{3}{19}}\psi_4 + \sqrt{\frac{5}{19}}\psi_5$$

If energy is measured on a large number of identical systems that are all initially in same state ψ,What values would we obtained with what probebilties?

Solution

According to orthonormality condition

$$\int_{-\infty}^{+\infty} {\psi_m}^* \, \psi_n dv = \delta_{mn}$$

δ_{mn} is called kronecker delta. Where $\delta_{mn} = \begin{cases} 0 & if\ m \neq n \\ 1 & if\ m = n \end{cases}$ So

$$\int_{-\infty}^{+\infty} \left(\frac{\mathbf{1}}{\sqrt{\mathbf{19}}}\boldsymbol{\psi_1} + \frac{\mathbf{2}}{\sqrt{\mathbf{19}}}\boldsymbol{\psi_2} + \sqrt{\frac{\mathbf{2}}{\mathbf{19}}}\boldsymbol{\psi_3} + \sqrt{\frac{\mathbf{3}}{\mathbf{19}}}\boldsymbol{\psi_4} + \sqrt{\frac{\mathbf{5}}{\mathbf{19}}}\boldsymbol{\psi_5}\right)^* \left(\frac{\mathbf{1}}{\sqrt{\mathbf{19}}}\boldsymbol{\psi_1} + \frac{\mathbf{2}}{\sqrt{\mathbf{19}}}\boldsymbol{\psi_2} + \sqrt{\frac{\mathbf{2}}{\mathbf{19}}}\boldsymbol{\psi_3} + \sqrt{\frac{\mathbf{3}}{\mathbf{19}}}\boldsymbol{\psi_4} + \sqrt{\frac{\mathbf{5}}{\mathbf{19}}}\boldsymbol{\psi_5}\right) dx$$

$$\int_{-\infty}^{+\infty} \left(\frac{\mathbf{1}}{\sqrt{\mathbf{19}}} \times \frac{\mathbf{1}}{\sqrt{\mathbf{19}}}\boldsymbol{\psi_1}^*\boldsymbol{\psi_1} + \frac{\mathbf{2}}{\sqrt{\mathbf{19}}} \times \frac{\mathbf{2}}{\sqrt{\mathbf{19}}}\boldsymbol{\psi_2}^*\boldsymbol{\psi_2} + \sqrt{\frac{\mathbf{2}}{\mathbf{19}}} \times \sqrt{\frac{\mathbf{2}}{\mathbf{19}}}\boldsymbol{\psi_3}^*\boldsymbol{\psi_3} + \sqrt{\frac{\mathbf{3}}{\mathbf{19}}} \times \sqrt{\frac{\mathbf{3}}{\mathbf{19}}}\boldsymbol{\psi_4}^*\boldsymbol{\psi_4} + \sqrt{\frac{\mathbf{5}}{\mathbf{19}}} \times \sqrt{\frac{\mathbf{5}}{\mathbf{19}}}\boldsymbol{\psi_5}^*\boldsymbol{\psi_5}\right) \boldsymbol{d}$$

$$= \frac{\mathbf{1}}{\mathbf{19}} + \frac{\mathbf{4}}{\mathbf{19}} + \frac{\mathbf{2}}{\mathbf{19}} + \frac{\mathbf{3}}{\mathbf{19}} + \frac{\mathbf{5}}{\mathbf{19}} = \frac{\mathbf{15}}{\mathbf{19}}$$

Now probability of energy of state $\boldsymbol{\psi_1}$

$$P(E_1) = \frac{\left|\int_{-\infty}^{+\infty} {\psi_1}^* \left(\frac{1}{\sqrt{19}}\psi_1 + \frac{2}{\sqrt{19}}\psi_2 + \sqrt{\frac{2}{19}}\psi_3 + \sqrt{\frac{3}{19}}\psi_4 + \sqrt{\frac{5}{19}}\psi_5\right) dx\right|^2}{\int_{-\infty}^{+\infty} {\psi_m}^* \, \psi_n dx}$$

$$P(E_1) = \frac{\left|\frac{1}{\sqrt{19}} \times \frac{1}{\sqrt{19}}\right|^2}{\frac{\mathbf{15}}{\mathbf{19}}} = \frac{1}{15}$$

Now probability of energy of state $\boldsymbol{\psi_2}$

$$P(E_1) = \frac{\left|\int_{-\infty}^{+\infty} {\psi_2}^* \left(\frac{1}{\sqrt{19}}\psi_1 + \frac{2}{\sqrt{19}}\psi_2 + \sqrt{\frac{2}{19}}\psi_3 + \sqrt{\frac{3}{19}}\psi_4 + \sqrt{\frac{5}{19}}\psi_5\right) dx\right|^2}{\int_{-\infty}^{+\infty} {\psi_m}^* \, \psi_n dx}$$

$$P(E_2) = \frac{\left|\frac{2}{\sqrt{19}} \times \frac{2}{\sqrt{19}}\right|^2}{\frac{\mathbf{15}}{\mathbf{19}}} = \frac{2}{15}$$

Similarly

$P(E_3) = \frac{2}{15}$, $P(E_4) = \frac{3}{15}$, $P(E_5) = \frac{5}{15}$

4. Show that $\boldsymbol{\psi}_{(x)} = \boldsymbol{e}^{-\frac{x^2}{2}}$ is an Eigen function of the operator $\frac{\partial^2}{\partial x^2} - x^2$. Find the corresponding Eigen value?

Solution

Here operator $\hat{A} = \frac{\partial^2}{\partial x^2} - x^2$

As Eigen value equation is

$$\hat{A}\psi_{(x)} = a\psi_{(x)}$$

So

$$\left(\frac{\partial^2}{\partial x^2} - x^2\right)\boldsymbol{e}^{-\frac{x^2}{2}} = \frac{\partial^2 \boldsymbol{e}^{-\frac{x^2}{2}}}{\partial x^2} - x^2\boldsymbol{e}^{-\frac{x^2}{2}} = \frac{\partial}{\partial x}\left(\frac{-2x}{2}\right)\boldsymbol{e}^{-\frac{x^2}{2}} - x^2\boldsymbol{e}^{-\frac{x^2}{2}}$$

$$= -\boldsymbol{e}^{-\frac{x^2}{2}} - \left(\frac{-2x}{2}\right)\boldsymbol{x}\boldsymbol{e}^{-\frac{x^2}{2}} - x^2\boldsymbol{e}^{-\frac{x^2}{2}} = -\boldsymbol{e}^{-\frac{x^2}{2}} = -\psi_{(x)}$$

So $\psi_{(x)}$ is Eigen function of the operator $\hat{A} = \frac{\partial^2}{\partial x^2} - x^2$ with corresponding Eigen value -1.

5. Check whether or not the following operators are linear or not?

a. $\frac{d}{dx}$ b. Sin c. $\sqrt{}$

Solution

a. Let ψ_1 and ψ_2 are two arbitrary wave functions

Then according to definition of linear operator $\hat{A}$

$$\hat{A}(a\psi_1 + b\psi_2) = a\hat{A}\psi_1 + b\hat{A}\psi_2$$

Here $\hat{A} = \frac{d}{dx}$ so

$$\frac{d}{dx}(a\psi_1 + b\psi_2) = a\frac{d}{dx}\psi_1 + b\frac{d}{dx}\psi_2$$

Hence $\frac{d}{dx}$ is linear.

b. $$\mathrm{Sin}(a\psi_1 + b\psi_2) \neq aSin\psi_1 + bSin\psi_2$$

Hence Sin is not linear.

c. $$\sqrt{(a\psi_1 + b\psi_2)} \neq \sqrt{a\psi_1} + \sqrt{b\psi_2}$$

Hence √ is not linear.

6. Show that if two operators are compatible then they commute each other or Show that if two operators $\hat{A}$ and $\hat{B}$ have same Eigen function then they commute each other?

Solution

Now by definition of Eigen value equation

$$\hat{A}\psi = a\psi \qquad \text{And} \qquad \hat{B}\psi = b\psi$$

Now

$$\hat{A}\hat{B}\psi - \hat{B}\hat{A}\psi = b\hat{A}\psi - a\hat{B}\psi = ba\psi - ab\psi = ab\psi - ab\psi = 0$$

$$\Rightarrow \hat{A}\hat{B}\psi - \hat{B}\hat{A}\psi = \left[\hat{A}, \hat{B}\right]\psi = 0$$

$$\Rightarrow \hat{A}\hat{B} - \hat{B}\hat{A} = \left[\hat{A}, \hat{B}\right] = 0$$

Hence $\hat{A}$ and $\hat{B}$ Commute each other.

7. For any two operators $\hat{A}$ and $\hat{B}$, show that

a. $\left(\overset{\dagger}{\hat{A}}\right)^{\dagger} = \hat{A}$

b. $\left(\hat{A}\hat{B}\right)^{\dagger} = \overset{\dagger}{\hat{\boldsymbol{B}}}\overset{\dagger}{\hat{A}}$

Solution

a. By definition

$$\int_{-\infty}^{+\infty} \phi^* \overset{\dagger}{\hat{\boldsymbol{B}}}\psi dx = \int_{-\infty}^{+\infty} \overset{*}{\hat{\boldsymbol{B}}}\phi^* \psi dx$$

Put $\hat{\boldsymbol{B}} = \overset{\dagger}{\hat{A}}$

$$\int_{-\infty}^{+\infty} \phi^* \left(\overset{\dagger}{\overset{\dagger}{\hat{A}}}\right)\psi dx = \int_{-\infty}^{+\infty} \left(\overset{*}{\overset{\dagger}{\hat{A}}}\right)\phi^* \psi dx$$

So $$\left(\overset{\dagger}{\hat{A}}\right)^{\dagger} = \hat{A}$$

b. By definition

$$\int_{-\infty}^{+\infty} \phi^* \left(\hat{A}\hat{B}\right)^{\dagger} \psi dx = \int_{-\infty}^{+\infty} \left(\hat{A}\hat{B}\right)^{*} \phi^* \psi dx$$

$$\int_{-\infty}^{+\infty} \phi^* \left(\hat{A}\hat{B}\right)^{\dagger} \psi dx = \int_{-\infty}^{+\infty} \phi^* \overset{\dagger\,\dagger}{\hat{B}}\hat{A}\psi dx$$

So $$\left(\hat{A}\hat{B}\right)^{\dagger} = \overset{\dagger\,\dagger}{\hat{\boldsymbol{B}}}\hat{A}$$

8. Show that linear combination of two Eigen functions of a Hermitian operator$\hat{A}$ is also an Eigen function of $\hat{A}$ with same Eigen value?

Solution

Let ψ_1 and ψ_2 are the Eigen functions of the same operator $\hat{A}$ with same Eigen value λ. So we can write

$$\hat{A}\psi_1 = \lambda\psi_1$$
$$\hat{A}\psi_2 = \lambda\psi_2$$

Now we take a linear combination of ψ_1 and ψ_2 and operate$\hat{A}$.

$$\hat{A}(a\psi_1 + b\psi_2) = \left(a\hat{A}\psi_1 + b\hat{A}\psi_2\right)$$
$$= a\lambda\psi_1 + b\lambda\psi_2 = \lambda(a\psi_1 + b\psi_2)$$

This result shows that linear combination of two Eigen functions ψ_1 and $\psi_2$of a hermitian operator$\hat{A}$ is also an Eigen function of $\hat{A}$ with same Eigen value.

9. Prove that total probability density of a wave function is constant if and only if the Hamiltonian of the system is Hermitian?

Solution

As probability density is

$$P = \int_{-\infty}^{+\infty} \psi^* \psi \, dx$$

Probability will be constant when

$$\frac{dP}{dt} = 0$$

$$\frac{dP}{dt} = \frac{d}{dt}\int_{-\infty}^{+\infty} \psi^* \psi \, dx$$

$$\Rightarrow \frac{dP}{dt} = \int_{-\infty}^{+\infty} \left(\frac{d\psi^*}{dt}\psi + \psi^* \frac{d\psi}{dt}\right) dx \text{------ (1)}$$

Now time dependent Schrodinger's equation is

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$$

$$\frac{\partial \psi}{\partial t} = \frac{\hat{H}\psi}{i\hbar}$$

By complex conjugate $\frac{\partial \psi^*}{\partial t} = \frac{-(\hat{H}\psi)^*}{i\hbar}$

Substitute vales of $\frac{\partial \psi}{\partial t}$ and $\frac{\partial \psi^*}{\partial t}$ in equation 1

$$\frac{dP}{dt} = \int_{-\infty}^{+\infty} \left(\frac{-\left(\hat{H}\psi\right)^*}{i\hbar}\psi + \psi^* \frac{\hat{H}\psi}{i\hbar}\right) dx$$

$$\frac{dP}{dt} = \int_{-\infty}^{+\infty} \left(-\psi^* \overset{\dagger}{\hat{H}}\psi + \psi^* \hat{H}\psi\right) d$$

$$\frac{dP}{dt} = -\int_{-\infty}^{+\infty} \psi^* \overset{\dagger}{\hat{H}}\psi \, dx + \int_{-\infty}^{+\infty} \psi^* \hat{H}\psi \, dx$$

For Hermitian operator $\overset{\dagger}{\hat{H}} = \hat{H}$

$$\frac{dP}{dt} = -\int_{-\infty}^{+\infty} \psi^* \hat{H}\psi \, dx + \int_{-\infty}^{+\infty} \psi^* \hat{H}\psi \, dx$$

$$\Rightarrow \frac{dP}{dt} = 0$$

$$\Rightarrow P = constant$$

10. Prove that if two Hermitian operators $\hat{A}$ and $\hat{B}$ commute and has no degenerate Eigen value then each Eigen vector of $\hat{A}$ will be the eigen vector of $\hat{B}$.Moreover, we can construct a common orthonormal basis that is made by the joint Eigen vectors of $\hat{A}$ and $\hat{B}$?

Solution

Now by Eigen value equation

$$\hat{A}\,\psi = a\psi \text{----- (1)}$$

For commuting operators

$$\hat{A}\,\hat{B}\psi = \hat{B}\hat{A}\psi$$

$$\Rightarrow \hat{A}\,\hat{B}\psi = a\left(\hat{B}\psi\right)$$

This equation shows that $\hat{B}\psi$ is Eigen of vector$\hat{A}$ corresponding to Eigen value a. Since Eigen vector is unique so ψ must be the Eigen vector of $\hat{B}$ i.e

$$\hat{B}\,\psi = b\psi$$

Hence Eigen vector of $\hat{A}$ is also an Eigen vector of $\hat{B}$.Hence we can construct a common orthonormal basis made by the joint Eigen vectors of $\hat{A}$ and $\hat{B}$.

11. Show that Eigen values of anti-Hermitian operators are pure imaginary or zero.?

    Solution

    By definition of anti-Hermitian operator $\hat{A}$

$$\hat{A}^{\dagger} = -\hat{A}$$

Now Eigen value equation is

$$\hat{A}\,\psi = a\psi \text{-----(1)}$$

By Taking complex conjugate

$$\left(\hat{A}\,\psi\right)^{*} = (a\psi)^{*} \text{-----(2)}$$

Multiply equation 1 with ψ^{*} and integrate

$$\int_{-\infty}^{+\infty} \psi^{*}\hat{A}\,\psi dx = \int_{-\infty}^{+\infty} a\psi^{*}\psi dx \text{-----(3)}$$

Multiply equation 2 with ψ and integrate

$$\int_{-\infty}^{+\infty} \left(\hat{A}\,\psi\right)^{*}\psi dx = \int_{-\infty}^{+\infty} (a\psi)^{*}\psi dx$$

$$\int_{-\infty}^{+\infty} \psi^{*}\hat{A}^{\dagger}\psi dx = \int_{-\infty}^{+\infty} a^{*}\psi^{*}\psi dx$$

As for anti-Hermitian operator $\hat{A}$

$$\hat{A}^{\dagger} = -\hat{A}$$

So

$$-\int_{-\infty}^{+\infty} \psi^* \hat{A}\, \psi dx = \int_{-\infty}^{+\infty} a^* \psi^* \psi dx \text{ ---- (4)}$$

Add equation 3 and 4 we get

$$0 = \int_{-\infty}^{+\infty} (a + a^*)\psi^* \psi dx$$

$$\Rightarrow a + a^* = 0$$

$$\Rightarrow a = -a^*$$

Let $a = x + iy$ then $a^* = x - iy$

$$\Rightarrow a = -a^* = x + iy = -x + iy$$

$$\Rightarrow 2x = 0 \Rightarrow x = 0$$

As $$a = x + iy \Rightarrow a = iy$$

So, Eigen values of anti-Hermitian operators are pure imaginary or zero.

12. Show that position operator is Hermitian?

    Solution

Let $\hat{r}$ is a position operator then we know that for Hermitian operator

$$\int_{-\infty}^{+\infty} \phi^* \overset{\dagger}{\hat{\boldsymbol{r}}} \psi dr = \int_{-\infty}^{+\infty} \overset{*}{\hat{\boldsymbol{r}}} \phi^* \psi dr$$

But $\overset{*}{\hat{r}} = \hat{r}$ so

$$\int_{-\infty}^{+\infty} \phi^* \overset{\dagger}{\hat{\boldsymbol{r}}} \psi dr = \int_{-\infty}^{+\infty} \hat{\boldsymbol{r}} \phi^* \psi dr = \int_{-\infty}^{+\infty} \phi^* \hat{\boldsymbol{r}} \psi dr$$

$$\overset{\dagger}{\hat{\boldsymbol{r}}} = \hat{\boldsymbol{r}}$$

Hence Position operator is Hermitian operator.

13. Assuming wave function vanishes to infinity then show that momentum operator is Hermitian operator?

    Solution

Let $\hat{P}$ is a position operator then we know that for Hermitian operator

$$\int_{-\infty}^{+\infty} \phi^* \overset{\dagger}{\widehat{\boldsymbol{P}}} \psi dr = \int_{-\infty}^{+\infty} \overset{*}{\widehat{\boldsymbol{P}}} \phi^* \psi dr$$

$$\int_{-\infty}^{+\infty} \phi^* \overset{\dagger}{\widehat{\boldsymbol{P}}} \psi dr = \int_{-\infty}^{+\infty} (-i\hbar\nabla)^* \phi^* \psi dr$$

$$\int_{-\infty}^{+\infty} \phi^* \overset{\dagger}{\widehat{\boldsymbol{P}}} \psi dr = +i\hbar \int_{-\infty}^{+\infty} \frac{d\phi^*}{dr} \psi dr$$

Integration by parts on right side of above equation

$$\int_{-\infty}^{+\infty} \phi^* \overset{\dagger}{\widehat{\boldsymbol{P}}} \psi dr = i\hbar \left\{ |\phi^* \psi|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \phi^* \frac{d\psi}{dr} dr \right\}$$

$$\int_{-\infty}^{+\infty} \phi^* \overset{\dagger}{\widehat{\boldsymbol{P}}} \psi dr = i\hbar \left\{ |\phi^* \psi|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \phi^* \frac{d\psi}{dr} dr \right\}$$

$$\int_{-\infty}^{+\infty} \phi^* \overset{\dagger}{\widehat{\boldsymbol{P}}} \psi dr = 0 - i\hbar \int_{-\infty}^{+\infty} \phi^* \frac{d\psi}{dr} dr = \int_{-\infty}^{+\infty} \phi^* \left(-i\hbar \frac{d}{dr}\right) \psi dr$$

$$\int_{-\infty}^{+\infty} \phi^* \overset{\dagger}{\widehat{\boldsymbol{P}}} \psi dr = \int_{-\infty}^{+\infty} \phi^* (-i\hbar\nabla)\, \psi dr = \int_{-\infty}^{+\infty} \phi^* \hat{P}\, \psi dr$$

$$\Rightarrow \overset{\dagger}{\widehat{\boldsymbol{P}}} = \hat{P}$$

Hence momentum operator is Hermitian.

14. If the operators $\hat{A}$ and $\hat{B}$ are Hermitian then which one of the following operator is hermitian?

a. $i\left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)$

b. $\hat{A}\hat{B} - \hat{B}\hat{A}$

c. $\frac{\hat{A}\hat{B}+\hat{B}\hat{A}}{2}$

Solution

a. $i\left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)$

Take Hermitian conjugate

$$\left\{i\left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)\right\}^\dagger = -i\left\{\left(\hat{A}\hat{B}\right)^\dagger - \left(\hat{B}\hat{A}\right)^\dagger\right\}$$

$$\{i(\hat{A}\hat{B}-\hat{B}\hat{A})\}^{\dagger}=-i\{\hat{B}^{\dagger}\hat{A}^{\dagger}-\hat{A}^{\dagger}\hat{B}^{\dagger}\}$$

As $\hat{A}$ and $\hat{B}$ are Hermitian,So $\hat{A}^{\dagger}=\hat{A}$ and $\hat{B}^{\dagger}=\hat{B}$.There fore

$$\{i(\hat{A}\hat{B}-\hat{B}\hat{A})\}^{\dagger}=-i\{\hat{B}\hat{A}-\hat{A}\hat{B}\}$$

$$\Rightarrow i(\hat{A}\hat{B}-\hat{B}\hat{A})^{\dagger}=i(\hat{A}\hat{B}-\hat{B}\hat{A})$$

Hence the operator $i(\hat{A}\hat{B}-\hat{B}\hat{A})$ is Hermitian.

b. $\hat{A}\hat{B}-\hat{B}\hat{A}$

Take Hermitian conjugate

$$(\hat{A}\hat{B}-\hat{B}\hat{A})^{\dagger}=(\hat{A}\hat{B})^{\dagger}-(\hat{B}\hat{A})^{\dagger}=\hat{B}^{\dagger}\hat{A}^{\dagger}-\hat{A}^{\dagger}\hat{B}^{\dagger}$$

As $\hat{A}$ and $\hat{B}$ are Hermitian,So $\hat{A}^{\dagger}=\hat{A}$ and $\hat{B}^{\dagger}=\hat{B}$.There fore

$$(\hat{A}\hat{B}-\hat{B}\hat{A})^{\dagger}=\hat{B}\hat{A}\ -\hat{A}\,\hat{B}=-(\hat{A}\hat{B}-\hat{B}\hat{A})$$

So $\hat{A}\hat{B}-\hat{B}\hat{A}$ is not Hermitian but skew Hermitian.

c. $\frac{\hat{A}\hat{B}+\hat{B}\hat{A}}{2}$

Take Hermitian conjugate

$$\left\{\frac{\hat{A}\hat{B}+\hat{B}\hat{A}}{2}\right\}^{\dagger}=\frac{(\hat{A}\hat{B})^{\dagger}+(\hat{B}\hat{A})^{\dagger}}{2}=\frac{\hat{B}^{\dagger}\hat{A}^{\dagger}+\hat{A}^{\dagger}\hat{B}^{\dagger}}{2}$$

$$\left\{\frac{\hat{A}\hat{B}+\hat{B}\hat{A}}{2}\right\}^{\dagger}=\frac{\hat{B}^{\dagger}\hat{A}^{\dagger}+\hat{A}^{\dagger}\hat{B}^{\dagger}}{2}$$

As $\hat{A}$ and $\hat{B}$ are Hermitian,So $\hat{A}^{\dagger}=\hat{A}$ and $\hat{B}^{\dagger}=\hat{B}$.There fore

$$\left\{\frac{\hat{A}\hat{B}+\hat{B}\hat{A}}{2}\right\}^{\dagger}=\frac{\hat{B}\hat{A}+\hat{A}\hat{B}}{2}=\frac{\hat{A}\hat{B}+\hat{B}\hat{A}}{2}$$

Hence $\frac{\hat{A}\hat{B}+\hat{B}\hat{A}}{2}$ is Hermitian.

15. If $\hat{A}$ is Hermitian then show that$\langle\hat{A}^2\rangle\geq 0$?

Solution

We know that

$$\langle\hat{A}^2\rangle=\int_{-\infty}^{+\infty}\psi^{*}(\hat{A}\hat{A})\,\psi dr$$

Since $\hat{A}$ is Hermitian so, $\hat{A} = \hat{A}^{\dagger}$

$$\langle \hat{A}^2 \rangle = \int_{-\infty}^{+\infty} \psi^* \left(\hat{A}^{\dagger}\hat{A}\right) \psi dr = \int_{-\infty}^{+\infty} \left(\hat{A}\psi\right)^* \hat{A}\,\psi dr = \int_{-\infty}^{+\infty} \left(\hat{A}\psi\right)^* \left(\hat{A}\psi\right) dr$$

$$\langle \hat{A}^2 \rangle = \int_{-\infty}^{+\infty} \left|\hat{A}\psi\right|^2 dr \geq 0$$

$$\Rightarrow \langle \hat{A}^2 \rangle \geq 0$$

16. If $\hat{A}$ is Hermitian then show that $\langle \hat{A} \rangle^* = \langle \hat{A} \rangle$?

Solution

By definition

$$\langle \hat{A} \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{A}\,\psi dr$$

Taking complex conjugate

$$\langle \hat{A} \rangle^* = \int_{-\infty}^{+\infty} \psi^* \hat{A}^{\dagger}\,\psi dr$$

Since $\hat{A}$ is Hermitian so, $\hat{A} = \hat{A}^{\dagger}$

$$\langle \hat{A} \rangle^* = \int_{-\infty}^{+\infty} \psi^* \hat{A}\,\psi dr$$

$$\Rightarrow \langle \hat{A} \rangle^* = \langle \hat{A} \rangle$$

17. Show that any operator can be expressed in the form of linear combination of a Hermitian and skew Hermitian operators?

Solution

Let $\hat{A}$ is an operator then their Hermitian and skew Hermitian combinations can be written as

$$\hat{C} = \frac{\hat{A}+\hat{A}^{\dagger}}{2} \text{----- (1)}$$

$$\hat{D} = \frac{\hat{A}-\hat{A}^{\dagger}}{2} \text{----- (2)}$$

Add 1 and 2

$$\hat{C} + \hat{D} = \hat{A} + \hat{A}^{\dagger} + \hat{A} - \hat{A}^{\dagger}$$

$$\Rightarrow \hat{A} = \hat{C} + \hat{D}$$

Hence operator $\hat{A}$ can be expressed in the form of linear combination of Hermitian and skew Hermitian operators.

18. If $\hat{A}$, $\hat{B}$ and $\hat{C}$ are three different operators then show that

a. $[\hat{A} + \hat{B}, \hat{C}] = [\hat{A}, \hat{C}] + [\hat{B}, \hat{C}]$

b. $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$

Solution

a. $[\hat{A} + \hat{B}, \hat{C}] = [\hat{A}, \hat{C}] + [\hat{B}, \hat{C}]$

Take right hand side and Multiply with ψ

$$[\hat{A}, \hat{C}]\psi + [\hat{B}, \hat{C}]\psi = (\hat{A}\hat{C} - \hat{C}\hat{A})\psi + (\hat{B}\hat{C} - \hat{C}\hat{B})\psi$$

$$[\hat{A}, \hat{C}]\psi + [\hat{B}, \hat{C}]\psi = \hat{A}\hat{C}\psi - \hat{C}\hat{A}\psi + \hat{B}\hat{C}\psi - \hat{C}\hat{B}\psi$$

$$= (\hat{A} + \hat{B})\hat{C}\psi - \hat{C}(\hat{A} + \hat{B})\psi$$

$$= [\hat{A} + \hat{B}, \hat{C}]\psi$$

$$\Rightarrow [\hat{A} + \hat{B}, \hat{C}] = [\hat{A}, \hat{C}] + [\hat{B}, \hat{C}]$$

b. $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$

Take left hand side and multiply with ψ

$$[\hat{A}\hat{B}, \hat{C}]\psi = (\hat{A}\hat{B}\hat{C} - \hat{C}\hat{A}\hat{B})\psi$$

Add and subtract $\hat{A}\hat{C}\hat{B}$

$$[\hat{A}\hat{B}, \hat{C}]\psi = (\hat{A}\hat{B}\hat{C} + \hat{A}\hat{C}\hat{B} - \hat{A}\hat{C}\hat{B} - \hat{C}\hat{A}\hat{B})\psi$$

$$[\hat{A}\hat{B}, \hat{C}]\psi = \hat{A}(\hat{B}\hat{C} - \hat{C}\hat{B})\psi + (\hat{A}\hat{C} - \hat{C}\hat{A})\hat{B}\psi$$

$$\Rightarrow [\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$$

19. If If $\hat{A}$, $\hat{B}$ are Hermitian operators and $[\hat{A}, \hat{B}] = 0$ then show that the product $\hat{A}\hat{B}$ is also Hermitian?

Solution

By definition of Hermitian operator the product $\hat{A}\hat{B}$ will

$$\int_{-\infty}^{+\infty} \phi^* (\hat{A}\hat{B})^{\dagger} \psi dr = \int_{-\infty}^{+\infty} \phi^* (\hat{B}^{\dagger}\hat{A}^{\dagger}) \psi dr$$

$$\int_{-\infty}^{+\infty} \phi^* \left(\hat{A}\,\hat{B}\right)^{\dagger} \psi dr - \int_{-\infty}^{+\infty} \phi^* \left(\hat{B}^{\dagger}\hat{A}^{\dagger}\right) \psi dr = 0$$

$$\int_{-\infty}^{+\infty} \phi^* \left(\hat{A}\,\hat{B}\right)^{\dagger} \psi dr - \int_{-\infty}^{+\infty} \phi^* \left(\hat{B}\,\hat{A}\right) \psi dr = 0$$

By definition $\hat{A} = \hat{A}^{\dagger}$, $\hat{B} = \hat{B}^{\dagger}$ and $\hat{A}\hat{B} = \left(\hat{A}\,\hat{B}\right)^{\dagger}$

$$\int_{-\infty}^{+\infty} \phi^* \left(\hat{A}\,\hat{B}\right) \psi dr - \int_{-\infty}^{+\infty} \phi^* \left(\hat{B}\,\hat{A}\right) \psi dr = 0$$

$$\int_{-\infty}^{+\infty} \phi^* \left(\hat{A}\,\hat{B} - \hat{B}\,\hat{A}\right) \psi dr = 0$$

$$\Rightarrow \left(\hat{A}\,\hat{B} - \hat{B}\,\hat{A}\right) = 0$$

$$\Rightarrow \left[\hat{A}, \hat{B}\right] = 0$$

This shows product $\hat{A}\hat{B}$ is Hermitian.

20. Show that if $\left[\hat{H}, \hat{A}\right] = 0$ and $\frac{\partial \hat{A}}{\partial t} = 0$ then $\langle \Delta \hat{A} \rangle$ will be constant in time?

Solution

We know that Ehrenfest's theorem is

$$\frac{d < \hat{A} >}{dt} = \langle \frac{1}{i\hbar} \left[\hat{A}, \hat{H}\right] \rangle + \langle \frac{\partial \hat{A}}{\partial t} \rangle$$

$$\Rightarrow \frac{d\langle \Delta \hat{A} \rangle}{dt} = \langle \frac{1}{i\hbar} \left[\Delta \hat{A}, \hat{H}\right] \rangle + \langle \frac{\partial \Delta \hat{A}}{\partial t} \rangle$$

As $\Delta \hat{A} = \hat{A} - \langle \hat{A} \rangle$ so,

$$\frac{d\langle \Delta \hat{A} \rangle}{dt} = \langle \frac{1}{i\hbar} \left[\hat{A} - \langle \hat{A} \rangle, \hat{H}\right] \rangle + \langle \frac{\partial \left(\hat{A} - \langle \hat{A} \rangle\right)}{\partial t} \rangle$$

$$\Rightarrow \frac{d\langle \Delta \hat{A} \rangle}{dt} = \langle \frac{1}{i\hbar} \left[\hat{A}, \hat{H}\right] - \frac{1}{i\hbar} \left[\langle \hat{A} \rangle, \hat{H}\right] \rangle + \langle \frac{\partial \hat{A}}{\partial t} \rangle - \langle \frac{\partial \langle \hat{A} \rangle}{\partial t} \rangle$$

$$\Rightarrow \frac{d\langle \Delta \hat{A} \rangle}{dt} = \langle \frac{-1}{i\hbar} \left[\hat{H}, \hat{A}\right] + \frac{1}{i\hbar} \left[\hat{H}, \langle \hat{A} \rangle\right] \rangle + \langle \frac{\partial \hat{A}}{\partial t} \rangle - \langle \frac{\partial \langle \hat{A} \rangle}{\partial t} \rangle$$

As $\left[\hat{H}, \hat{A}\right] = 0$ and $\frac{\partial \hat{A}}{\partial t} = 0$ so,

$$\frac{d\langle \Delta \hat{A} \rangle}{dt} = 0$$

$$\Rightarrow \langle \Delta \hat{A} \rangle = constant$$

21. Show that for a wave packet moving in one dimension

$$m\frac{d < \hat{x}^2 >}{dt} = \langle \hat{x}\hat{P} \rangle + \langle \hat{P}\hat{x} \rangle$$

Solution

We know that Ehrenfest's theorem is

$$\frac{d < \hat{A} >}{dt} = \langle \frac{1}{i\hbar}\left[\hat{A}, \hat{H}\right] \rangle + \langle \frac{\partial \hat{A}}{\partial t} \rangle$$

$$\Rightarrow \frac{d < \hat{x}^2 >}{dt} = \langle \frac{1}{i\hbar}\left[\hat{x}^2, \hat{H}\right] \rangle + \langle \frac{\partial \hat{x}^2}{\partial t} \rangle$$

$$\Rightarrow \frac{d < \hat{x}^2 >}{dt} = \langle \frac{1}{i\hbar}\left[\hat{x}^2, \frac{\hat{P}^2}{2m}\right] \rangle + \langle \frac{\partial \hat{x}^2}{\partial t} \rangle$$

$$\Rightarrow \frac{d < \hat{x}^2 >}{dt} = \langle \frac{1}{2mi\hbar}\left[\hat{x}^2, \hat{P}\hat{P}\right] \rangle + \langle \frac{\partial \hat{x}^2}{\partial t} \rangle$$

$$\Rightarrow \frac{d < \hat{x}^2 >}{dt} = \langle \frac{i}{2m\hbar}\left[\hat{P}\hat{P}, \hat{x}^2\right] \rangle + \langle \frac{\partial \hat{x}^2}{\partial t} \rangle$$

$$\Rightarrow \frac{d < \hat{x}^2 >}{dt} = \langle \frac{i}{2m\hbar}\left\{\hat{P}\left[\hat{P}, \hat{x}^2\right] + \left[\hat{P}, \hat{x}^2\right]\hat{P}\right\} \rangle + \langle \frac{\partial \hat{x}^2}{\partial t} \rangle$$

$$\Rightarrow \frac{d < \hat{x}^2 >}{dt} = \langle \frac{i}{2m\hbar}\left\{\hat{P}\left(\left[\hat{P}, \hat{x}\right]\hat{x} + \hat{x}\left[\hat{P}, \hat{x}\right]\right) + \left(\left[\hat{P}, \hat{x}\right]\hat{x} + \hat{x}\left[\hat{P}, \hat{x}\right]\right)\hat{P}\right\} \rangle + \langle \frac{\partial \hat{x}^2}{\partial t} \rangle$$

$$\Rightarrow \frac{d < \hat{x}^2 >}{dt} = \langle \frac{i}{2m\hbar}\left\{\hat{P}(-i\hbar\hat{x} - i\hbar\hat{x}) + (-i\hbar\hat{x} - i\hbar\hat{x})\hat{P}\right\} \rangle + \langle \frac{\partial \hat{x}^2}{\partial t} \rangle$$

$$\Rightarrow \frac{d < \hat{x}^2 >}{dt} = \langle \frac{i}{2m\hbar}\left(-2i\hbar\hat{P}\hat{x} - 2i\hbar\hat{x}\hat{P}\right) \rangle + \langle \frac{\partial \hat{x}^2}{\partial t} \rangle$$

$$\Rightarrow \frac{d<\hat{x}^2>}{dt} = \langle\frac{1}{m}\left(\hat{P}\hat{x}+\hat{x}\hat{P}\right)\rangle + \langle\frac{\partial\hat{x}^2}{\partial t}\rangle$$

As $\hat{x}^2$ does not depends explicitly on time so, $\langle\frac{\partial\hat{x}^2}{\partial t}\rangle = 0$

$$\Rightarrow \frac{d<\hat{x}^2>}{dt} = \langle\frac{1}{m}\left(\hat{P}\hat{x}+\hat{x}\hat{P}\right)\rangle$$

$$\Rightarrow m\frac{d<\hat{x}^2>}{dt} = \langle\left(\hat{P}\hat{x}+\hat{x}\hat{P}\right)\rangle = \langle\hat{P}\hat{x}\rangle + \langle\hat{x}\hat{P}\rangle$$

22. For a particle moving in one dimension, show that $\hat{x}\hat{P}$ is not Hermitian.Construct an operator which corresponds to this physical observable product which is Hermitian?

    Solution

    Now according to definition of Hermitian operator

    $$\left(\hat{x}\hat{P}\right)^{\dagger} = \hat{P}^{\dagger}\hat{x}^{\dagger} \neq \hat{x}\hat{P}$$

    This result shows $\hat{x}\hat{P}$ is not Hermitian. Now we construct a Hermitian operator corresponding to $\hat{x}\hat{P}$.

    $$\left(\hat{x}\hat{P}+\hat{P}\hat{x}\right)^{\dagger} = \left(\hat{x}\hat{P}\right)^{\dagger} + \left(\hat{P}\hat{x}\right)^{\dagger} = \hat{P}^{\dagger}\hat{x}^{\dagger} + \hat{x}^{\dagger}\hat{P}^{\dagger}$$

    $$\left(\hat{x}\hat{P}+\hat{P}\hat{x}\right)^{\dagger} = \hat{x}^{\dagger}\hat{P}^{\dagger} + \hat{P}^{\dagger}\hat{x}^{\dagger}$$

    This result shows that operator $\hat{x}\hat{P}+\hat{P}\hat{x}$ is Hermitian.

23. Show that for an operator whose eigen value $\neq a^*$, then operator is not Hermitian?

    Solution

    Let $\hat{A}$ is an operator then its Eigen value equation is

    $$\hat{A}\,\psi = a\psi \text{----- (1)}$$

By Taking complex conjugate

$$\left(\hat{A}\,\psi\right)^{*} = (a\psi)^{*} \text{----- (2)}$$

Multiply equation 1 with ψ^* and integrate

$$\int_{-\infty}^{+\infty} \psi^* \hat{A}\, \psi dx = \int_{-\infty}^{+\infty} a\psi^* \psi dx \text{----- (3)}$$

Multiply equation 2 with ψ and integrate

$$\int_{-\infty}^{+\infty} \left(\hat{A}\, \psi\right)^* \psi dx = \int_{-\infty}^{+\infty} (a\psi)^* \psi dx$$

$$\int_{-\infty}^{+\infty} \psi^* \hat{A}^{\dagger} \psi dx = \int_{-\infty}^{+\infty} a^* \psi^* \psi dx \text{----- (4)}$$

Now if $\hat{A}$ is Hermitian $\hat{A}^{\dagger} = \hat{A}$ so

$$\int_{-\infty}^{+\infty} \psi^* \hat{A} \psi dx = \int_{-\infty}^{+\infty} a^* \psi^* \psi dx$$

$$\int_{-\infty}^{+\infty} \psi^* a \psi dx = \int_{-\infty}^{+\infty} a^* \psi^* \psi dx$$

$$\Rightarrow a = a^*$$

But we have given $a \neq a^*$ which shows $\hat{A}^{\dagger} \neq \hat{A}$

Hence operator $\hat{A}$ is not Hermitian.

24. A particle is in state $\psi = e^{-ax^2 - bt}$, where a and b are constants.

a. Is this state is stationary?

b. Find the expectation values of position and momentum of the particle?

c. Whether the result of b violates or not uncertainty principle?

Solution

a. We find the probability density of ψ

$$P = \psi^* \psi$$

$$P = e^{-ax^2 - bt} e^{-ax^2 - bt} = e^{-2ax^2 - 2bt}$$

As probability density is a function of time t so, this state is not stationary.

b. As expectation value

$$\langle \hat{x} \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{x} \psi dx$$

$$\langle \hat{x} \rangle = \int_{-\infty}^{+\infty} e^{-ax^2 - bt} \hat{x} e^{-ax^2 - bt} dx = \int_{-\infty}^{+\infty} \hat{x} e^{-2ax^2 - 2bt} dx = 0$$

Now

$$\langle \hat{P} \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{P} \psi dx$$

$$\langle \hat{P} \rangle = \int_{-\infty}^{+\infty} e^{-ax^2-bt} \left(-i\hbar \frac{d}{dx}\right) e^{-ax^2-bt} dx = -2i\hbar a \int_{-\infty}^{+\infty} \hat{x} e^{-2ax^2-2bt} dx = 0$$

c. As uncertainty principle is

$$\Delta \hat{x} \Delta \hat{P} \geq \hbar$$

$$\sqrt{\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2} \sqrt{\langle \hat{P}^2 \rangle - \langle \hat{P} \rangle^2} = \sqrt{\langle \hat{x}^2 \rangle} \sqrt{\langle \hat{P}^2 \rangle} \geq \hbar$$

$$\Rightarrow \Delta \hat{x} \Delta \hat{P} \geq \hbar$$

So, result of b $\langle \hat{x} \rangle = \langle \hat{P} \rangle = 0$ does not violates the uncertainty principal.

25. Normalized wave function of a particle is given by

$$\psi = \frac{1}{\sqrt{a\sqrt{\pi}}} e^{\frac{x^2}{2a^2}} e^{\frac{iP_o x}{\hbar}}$$

a. Where is the particle most likely to be found?

b. Find$\langle \hat{P} \rangle$?

Solution

a. Probability for finding the particle is

$$P = \psi^* \psi$$

$$P = \frac{1}{\sqrt{a\sqrt{\pi}}} e^{\frac{x^2}{2a^2}} e^{\frac{-iP_o x}{\hbar}} \frac{1}{\sqrt{a\sqrt{\pi}}} e^{\frac{x^2}{2a^2}} e^{\frac{iP_o x}{\hbar}} = \frac{1}{\sqrt{a\sqrt{\pi}}} e^{\frac{2x^2}{2a^2}} = \frac{1}{\sqrt{a\sqrt{\pi}}} e^{\frac{x^2}{a^2}}$$

b. Expectation value of momentum is

$$\langle \hat{P} \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{P} \psi dx$$

$$\langle \hat{P} \rangle = \int_{-\infty}^{+\infty} \frac{1}{\sqrt{a\sqrt{\pi}}} e^{\frac{x^2}{2a^2}} e^{\frac{-iP_o x}{\hbar}} \left(-i\hbar \frac{d}{dx}\right) \frac{1}{\sqrt{a\sqrt{\pi}}} e^{\frac{x^2}{2a^2}} e^{\frac{iP_o x}{\hbar}} dx$$

$$\langle \hat{P} \rangle = \frac{-i\hbar}{a\sqrt{\pi}} \int_{-\infty}^{+\infty} e^{\frac{x^2}{a^2}} e^{\frac{-iP_o x}{\hbar}} \left(\frac{iP_o}{\hbar} e^{\frac{iP_o x}{\hbar}} e^{\frac{x^2}{2a^2}} + \frac{x}{a^2} e^{\frac{x^2}{2a^2}} e^{\frac{iP_o x}{\hbar}}\right) dx$$

$$\langle \hat{P} \rangle = \frac{-i\hbar}{a\sqrt{\pi}} \int_{-\infty}^{+\infty} \left(\frac{iP_o}{\hbar} e^{\frac{x^2}{a^2}} + \frac{x}{a^2} e^{\frac{x^2}{a^2}} \right) dx = \frac{-i\hbar}{a\sqrt{\pi}} \int_{-\infty}^{+\infty} e^{\frac{x^2}{a^2}} \left(\frac{iP_o}{\hbar} + \frac{x}{a^2} \right) dx$$

$$\langle \hat{P} \rangle = \frac{-i\hbar}{a\sqrt{\pi}} \int_{-\infty}^{+\infty} \frac{iP_o}{\hbar} e^{\frac{x^2}{a^2}} dx + \frac{-i\hbar}{a\sqrt{\pi}} \int_{-\infty}^{+\infty} \frac{x}{a^2} e^{\frac{x^2}{a^2}} dx$$

$$\langle \hat{P} \rangle = \frac{-i\hbar}{a\sqrt{\pi}} \frac{iP_o}{\hbar} \left(a\sqrt{\pi} \right) + 0 = P_o$$

26. Show that a set of orthonormal functions is linearly independent?

Solution

Let $\psi_1, \psi_2 \; and \; \psi_n$ are orthonormal functions then their linear combination can be written as

$$a_1\psi_1 + a_2\psi_2 + a_3\psi_3 + - - - + a_n\psi_n = 0$$

Multiply by ${\psi_i}^*$ and integrate over whole volume.

$$\int_{-\infty}^{+\infty} \left(a_1 {\psi_i}^* \psi_1 + a_2 {\psi_i}^* \psi_2 + a_3 {\psi_i}^* \psi_3 + - - - + a_n {\psi_i}^* \psi_n \right) dv = 0$$

As orthonormal condition is written as

$$\int_{-\infty}^{+\infty} {\psi_m}^* \, \psi_n dv = \delta_{mn}$$

δ_{mn} is called kronecker delta. Where $\delta_{mn} = \begin{cases} 0 & if \; m \neq n \\ 1 & if \; m = n \end{cases}$ So

$$a_1(0) + a_2(0) + a_3(0) + - - - + a_n(0) = 0$$

Hence the set of orthonormal functions is linearly independent.

27. Show that $\left[\hat{x}, \hat{H}\right] = i\hbar \frac{dx}{dt}$

Solution

$$\left[\hat{x}, \hat{H}\right]\psi = \left(\hat{x}\hat{H} - \hat{H}\hat{x}\right)\psi$$

$$\left[\hat{x}, \hat{H}\right]\psi = \left\{ \hat{x} \left(\frac{P^2}{2m} + V \right) - \left(\frac{P^2}{2m} + V \right) \hat{x} \right\} \psi$$

$$\left[\hat{x}, \hat{H}\right]\psi = \left(\hat{x} \frac{P^2}{2m} + \hat{x}V - \frac{P^2}{2m} \hat{x} - V\hat{x} \right) \psi$$

$$[\hat{x},\hat{H}]\psi = \left(\hat{x}\frac{P^2}{2m} - \frac{P^2}{2m}\hat{x}\right)\psi = \frac{1}{2m}[\hat{x},P^2]$$

$$[\hat{x},\hat{H}]\psi = \frac{1}{2m}[\hat{x},P^2]\psi = \frac{1}{2m}\{[\hat{x},\hat{P}]\hat{P}\psi + \hat{P}[\hat{x},\hat{P}]\psi\}$$

$$[\hat{x},\hat{H}]\psi = \frac{1}{2m}\{i\hbar\hat{P}\psi + i\hbar\hat{P}\psi\} = \frac{i\hbar\hat{P}\psi}{m} = \frac{i\hbar mv\psi}{m} = i\hbar v\psi$$

$$[\hat{x},\hat{H}]\psi = i\hbar\frac{dx}{dt}\psi$$

$$\Rightarrow [\hat{x},\hat{H}] = i\hbar\frac{dx}{dt}$$

28. Show that momentum of a free particle is constant of motion?

Solution

We know that $\hat{H} = \frac{P^2}{2m} + V$ for free particle V=o so, $\hat{H} = \frac{P^2}{2m}$

Now

$$[\hat{P},\hat{H}]\psi = (\hat{P}\hat{H} - \hat{H}\hat{P})\psi$$

$$[\hat{P},\hat{H}]\psi = \left(\hat{P}\frac{P^2}{2m} - \frac{P^2}{2m}\hat{P}\right)\psi = 0$$

This results show that Momentum of free particle commute with Hamiltonian. Hence momentum of free particle is constant of motion.

29. If $\hat{H} = \frac{P^2}{2m} + V$ then show that $\left[\hat{x},[\hat{x},\hat{H}]\right] = -\frac{\hbar^2}{m}$?

Solution

As we know that $[\hat{x},\hat{H}] = i\hbar\frac{dx}{dt} = i\hbar\frac{P}{m}$ so,

$$\left[\hat{x},[\hat{x},\hat{H}]\right] = \left[\hat{x},i\hbar\frac{\hat{P}}{m}\right] = \frac{i\hbar}{m}[\hat{x},\hat{P}] = \frac{i\hbar}{m}(i\hbar) = -\frac{\hbar^2}{m}$$

30. Hamiltonian of the charge particle in an electromagnetic field is

$$\hat{H} = \frac{1}{2m}\left(\hat{P} - \frac{e}{c}A(x)\right)^2 + e\Phi(x)$$

Show that $\frac{d\hat{x}}{dt} = \frac{1}{m}\left(\hat{P} - \frac{e}{c}A(x)\right)$

Solution

As $[\hat{x},\hat{H}] = i\hbar\frac{d\hat{x}}{dt}$

$$\frac{d\hat{x}}{dt}=\frac{1}{i\hbar}[\hat{x},\hat{H}]=\frac{1}{i\hbar}\left[\hat{x},\frac{1}{2m}\left(\hat{P}-\frac{e}{c}A(x)\right)^2+e\Phi(x)\right]$$

$$\frac{d\hat{x}}{dt}=\frac{1}{i\hbar}\left[\hat{x},\frac{1}{2m}\left(\hat{P}-\frac{e}{c}A(x)\right)^2\right]+\frac{1}{i\hbar}[\hat{x},e\Phi(x)]=\frac{1}{i2m\hbar}\left[\hat{x},\left(\hat{P}-\frac{e}{c}A(x)\right)^2\right]+0$$

$$\frac{d\hat{x}}{dt}=\frac{1}{i2m\hbar}\left[\hat{x},\left(\hat{P}-\frac{e}{c}A(x)\right)\left(\hat{P}-\frac{e}{c}A(x)\right)\right]$$

$$\frac{d\hat{x}}{dt}=\frac{1}{i2m\hbar}\left(\hat{P}-\frac{e}{c}A(x)\right)\left[\hat{x},\left(\hat{P}-\frac{e}{c}A(x)\right)\right]+\frac{1}{i2m\hbar}\left[\hat{x},\left(\hat{P}-\frac{e}{c}A(x)\right)\right]\left(\hat{P}-\frac{e}{c}A(x)\right)$$

$$\frac{d\hat{x}}{dt}=\frac{1}{i2m\hbar}\left(\hat{P}-\frac{e}{c}A(x)\right)\left\{[\hat{x},\hat{P}]-\left[\hat{x},\frac{e}{c}A(x)\right]\right\}+\frac{1}{i2m\hbar}\left\{[\hat{x},\hat{P}]-\left[\hat{x},\frac{e}{c}A(x)\right]\right\}\left(\hat{P}-\frac{e}{c}A(x)\right)$$

$$\frac{d\hat{x}}{dt}=\frac{1}{i2m\hbar}\left(\hat{P}-\frac{e}{c}A(x)\right)\{i\hbar-0\}+\frac{1}{i2m\hbar}\{i\hbar-0\}\left(\hat{P}-\frac{e}{c}A(x)\right)$$

$$\Rightarrow\frac{d\hat{x}}{dt}=\frac{1}{m}\left(\hat{P}-\frac{e}{c}A(x)\right)$$

31. If $\hat{A}$ and $\hat{B}$ are constant of motion then show that $[\hat{A},\hat{B}]$ is also a constant of motion?

Solution

When an operator is a constant of motion then it commutes with Hamiltonian i.e

$$[\hat{A},\hat{H}]=0 \text{ And } [\hat{B},\hat{H}]=0$$

Now

$$\left[[\hat{A},\hat{B}],\hat{H}\right]=\left[(\hat{A}\hat{B}-\hat{B}\hat{A}),\hat{H}\right]=[\hat{A}\hat{B},\hat{H}]-[\hat{B}\hat{A},\hat{H}]$$

$$\left[[\hat{A},\hat{B}],\hat{H}\right]=\hat{A}[\hat{B},\hat{H}]+[\hat{A},\hat{H}]\hat{B}-\hat{B}[\hat{A},\hat{H}]-[\hat{B},\hat{H}]\hat{A}$$

$$\text{As } [\hat{A},\hat{H}]=0 \text{ And } [\hat{B},\hat{H}]=0$$

$$\left[[\hat{A},\hat{B}],\hat{H}\right]=0$$

Hence $[\hat{A},\hat{B}]$ is constant of motion.

32. Show that $\hat{x}\hat{P}$ is not a self adjoint operator while $\hat{x}\hat{P}+\hat{P}\hat{x}$ is self adjoint operator?

Solution

As both $\hat{x}$ and $\hat{P}$ are self adjoint operators i.e $\hat{x}^{\dagger} = \hat{x}$ and $\hat{P}^{\dagger} = \hat{P}$

Now

$$\left(\hat{x}\hat{P}\right)^{\dagger} = \hat{P}^{\dagger}\hat{x}^{\dagger} \neq \hat{x}\hat{P}$$

So $\hat{x}\hat{P}$ is not a self adjoint operator. Now

$$\left(\hat{x}\hat{P} + \hat{P}\hat{x}\right)^{\dagger} = \left(\hat{x}\hat{P}\right)^{\dagger} + \left(\hat{P}\hat{x}\right)^{\dagger} = \hat{P}^{\dagger}\hat{x}^{\dagger} + \hat{x}^{\dagger}\hat{P}^{\dagger} = \hat{P}\hat{x} + \hat{x}\hat{P} = \hat{x}\hat{P} + \hat{P}\hat{x}$$

Hence $\hat{x}\hat{P} + \hat{P}\hat{x}$ is a self adjoint operator.

33. Show that complex conjugate is not a linear operator. Also show that the operator which changes to a function to its square is not a linear operator?

Solution

Consider an operator $\hat{A}$ changes a wave function ψ to its complex conjugate ψ^{*} as

$$\hat{A}\psi = \psi^{*}$$

Now we check linearity

$$\hat{A}(a_1\psi_1 + a_2\psi_2) = {a_1}^{*}{\psi_1}^{*} + {a_2}^{*}{\psi_2}^{*}$$

$$\hat{A}(a_1\psi_1 + a_2\psi_2) = {a_1}^{*}\left(\hat{A}\psi_1\right) + {a_2}^{*}\left(\hat{A}\psi_2\right)$$

$$\hat{A}(a_1\psi_1 + a_2\psi_2) \neq a_1\left(\hat{A}\psi_1\right) + a_2\left(\hat{A}\psi_2\right)$$

Hence complex conjugate is not a linear operator.

Now we consider another operator $\hat{B}$ which changes a wave function ψ to ψ^2

$$\hat{B}\psi = \psi^2$$

Now we check linearity

$$\hat{B}(a_1\psi_1 + a_2\psi_2) = (a_1\psi_1 + a_2\psi_2)^2 = {a_1}^2{\psi_1}^2 + {a_2}^2{\psi_2}^2 + 2a_1a_2\psi_1\psi_2$$

$$\hat{B}(a_1\psi_1 + a_2\psi_2) = {a_1}^2(\hat{B}\psi_1) + {a_2}^2(\hat{B}\psi_2) + 2a_1a_2\psi_1\psi_2$$

$$\hat{B}(a_1\psi_1 + a_2\psi_2) \neq a_1(\hat{B}\psi_1) + a_2(\hat{B}\psi_2)$$

Hence, operator$\hat{B}$ which changes a wave function to its square is non linear operator.

34. If $\hat{A}$ commute with $\hat{B}$ and $\hat{C}$ commute with $\hat{B}$ then show that $\hat{C}$and $\hat{A}$ may or may not commute?

Solution

When $\hat{A}$ commute with $\hat{B}$ then $[\hat{A}, \hat{B}] = 0$ and when $\hat{C}$ commutes with $\hat{B}$, $[\hat{C}, \hat{B}] = 0$

$$\Rightarrow [\hat{A}, \hat{B}] = (\hat{A}\hat{B} - \hat{B}\hat{A}) = 0 \Rightarrow \hat{A}\hat{B} = \hat{B}\hat{A}$$

And $$[\hat{C}, \hat{B}] = (\hat{C}\hat{B} - \hat{B}\hat{C}) = 0 \Rightarrow \hat{C}\hat{B} = \hat{B}\hat{C}$$

Now $$[\hat{A}, \hat{C}] = (\hat{A}\hat{C} - \hat{C}\hat{A}) \neq 0$$

So, this shows that $\hat{C}$and $\hat{A}$ may or may not commute.

35. If two operators $\hat{A}$ and $\hat{B}$ commute with their commutator i.e

$[\hat{A}, [\hat{A}, \hat{B}]] = 0$ And $[\hat{B}, [\hat{A}, \hat{B}]] = 0$ then show that

a. $[\hat{A}, \hat{B}^n] = n\hat{B}^{n-1}[\hat{A}, \hat{B}]$

b. $[\hat{A}^n, \hat{B}] = n\hat{A}^{n-1}[\hat{A}, \hat{B}]$

Solution

a. $[\hat{A}, \hat{B}^n] = n\hat{B}^{n-1}[\hat{A}, \hat{B}]$

Now $[\hat{A}, \hat{B}^n] = \hat{B}^{n-1}[\hat{A}, \hat{B}\,\hat{B}^{n-1}] = [\hat{A}, \hat{B}]\hat{B}^{n-1} + \hat{B}[\hat{A}, \hat{B}^{n-1}]$

$$\Rightarrow [\hat{A}, \hat{B}^n] = [\hat{A}, \hat{B}]\hat{B}^{n-1} + \hat{B}[\hat{A}, \hat{B}\hat{B}^{n-2}]$$

$$\Rightarrow [\hat{A}, \hat{B}^n] = [\hat{A}, \hat{B}]\hat{B}^{n-1} + \hat{B}[\hat{A}, \hat{B}]\hat{B}^{n-2} + \hat{B}\hat{B}[\hat{A}, \hat{B}^{n-2}]$$

$$\Rightarrow [\hat{A}, \hat{B}^n] = 2[\hat{A}, \hat{B}]\hat{B}^{n-1} + \hat{B}^2[\hat{A}, \hat{B}^{n-2}]$$

By performing same operation n times we get

$$\left[\hat{A}\,,\hat{B}^{n}\right]=n\left[\hat{A}\,,\hat{B}\right]\hat{B}^{n-1}+\hat{B}^{n}\left[\hat{A}\,,\hat{B}^{n-n}\right]$$

$$\Rightarrow\left[\hat{A}\,,\hat{B}^{n}\right]=n\left[\hat{A}\,,\hat{B}\right]\hat{B}^{n-1}+0=n\hat{B}^{n-1}\left[\hat{A}\,,\hat{B}\right]$$

b. $\left[\hat{A}^{\,n},\hat{B}\right]=n\hat{A}^{n-1}\left[\hat{A}\,,\hat{B}\right]$ Solution will be same as in part a.

36. If $\hat{A}$ and $\hat{B}$ are two Hermitian operators, then show that $\left[\hat{A}\,,\hat{B}\right]$ is anti Hermitian while, $i\left[\hat{A}\,,\hat{B}\right]$ is Hermitian?

Solution

As $$\left[\hat{A}\,,\hat{B}\right]=\hat{A}\,\hat{B}-\hat{B}\hat{A}$$

Take Hermitian conjugate on both sides

$$\left[\hat{A}\,,\hat{B}\right]^{\dagger}=\left(\hat{A}\,\hat{B}-\hat{B}\hat{A}\right)^{\dagger}=\left(\hat{A}\,\hat{B}\right)^{\dagger}-\left(\hat{B}\hat{A}\right)^{\dagger}$$

$$\left[\hat{A}\,,\hat{B}\right]^{\dagger}=\hat{B}^{\dagger}\hat{A}^{\dagger}-\hat{A}^{\dagger}\hat{B}^{\dagger}=\hat{B}\hat{A}-\hat{A}\hat{B}$$

$$\left[\hat{A}\,,\hat{B}\right]^{\dagger}=-\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right)=-\left[\hat{A}\,,\hat{B}\right]$$

So $\left[\hat{A}\,,\hat{B}\right]$ is anti Hermitian.

Now $$i\left[\hat{A}\,,\hat{B}\right]=i\hat{A}\,\hat{B}-i\hat{B}\hat{A}$$

Take Hermitian conjugate on both sides

$$\left(i\left[\hat{A}\,,\hat{B}\right]\right)^{\dagger}=\left(i\hat{A}\,\hat{B}-i\hat{B}\hat{A}\right)^{\dagger}=\left(i\hat{A}\,\hat{B}\right)^{\dagger}-\left(i\hat{B}\hat{A}\right)^{\dagger}$$

$$\left(i\left[\hat{A}\,,\hat{B}\right]\right)^{\dagger}=-i\hat{B}^{\dagger}\hat{A}^{\dagger}+i\hat{A}^{\dagger}\hat{B}^{\dagger}=-i\hat{B}\hat{A}+i\hat{A}\hat{B}$$

$$\left(i\left[\hat{A}\,,\hat{B}\right]\right)^{\dagger}=i\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right)=i\left[\hat{A}\,,\hat{B}\right]$$

So, $i\left[\hat{A}\,,\hat{B}\right]$ is Hermitian.

37. If two operators $\hat{A}$ and $\hat{B}$ commute with $\hat{C}$ then show that their commutator also commute with $\hat{C}$?

Solution

Given $\left[\hat{A}\,,\hat{C}\right]=0$ and $\left[\hat{B}\,,\hat{C}\right]=0$. We have to show that $\left[\left[\hat{A}\,,\hat{B}\right],\hat{C}\right]=0$

Now $\left[\left[\hat{A}\,,\hat{B}\right],\hat{C}\right]=\left[\hat{A}\,,\hat{B}\right]\hat{C}-\hat{C}\left[\hat{A}\,,\hat{B}\right]=\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right)\hat{C}-\hat{C}\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right)$

$$\left[\left[\hat{A}\,,\hat{B}\right],\hat{C}\right]=\left(\hat{A}\hat{B}\hat{C}-\hat{B}\hat{A}\hat{C}\right)-\left(\hat{C}\hat{A}\hat{B}-\hat{C}\hat{B}\hat{A}\right)$$

$$\left[\left[\hat{A}\,,\hat{B}\,\right],\hat{C}\right]=\hat{A}\hat{B}\hat{C}-\hat{B}\hat{A}\hat{C}-\hat{C}\hat{A}\hat{B}+\hat{C}\hat{B}\hat{A}$$

$$\left[\left[\hat{A}\,,\hat{B}\,\right],\hat{C}\right]=\hat{B}\left(\hat{A}\hat{C}-\hat{C}\hat{A}\right)+\hat{A}\left(\hat{B}\hat{C}-\hat{C}\hat{B}\right)$$

$$\left[\left[\hat{A}\,,\hat{B}\,\right],\hat{C}\right]=\hat{B}\left[\hat{A}\,,\hat{C}\,\right]+\hat{A}\left[\hat{B}\,,\hat{C}\,\right]=0$$

38. If $\hat{x}$ and $\hat{P}$ are the position and momentum operators respectively then show that $\left[\hat{x}\,,e^{\frac{-ia\hat{P}}{\hbar}}\right]=ae^{\frac{-ia\hat{P}}{\hbar}}$

Solution

AS $e^{\frac{-ia\hat{P}}{\hbar}}=\sum_{n=0}^{\infty}\frac{\left(\frac{-ia\hat{P}}{\hbar}\right)^n}{n!}$

Now $$\left[\hat{x}\,,e^{\frac{-ia\hat{P}}{\hbar}}\right]=\left[\hat{x}\,,\sum_{n=0}^{\infty}\frac{\left(\frac{-ia\hat{P}}{\hbar}\right)^n}{n!}\right]=\sum_{n=0}^{\infty}\frac{1}{n!}\left[\hat{x}\,,\left(\frac{-ia\hat{P}}{\hbar}\right)^n\right]$$

$$\left[\hat{x}\,,e^{\frac{-ia\hat{P}}{\hbar}}\right]=[\hat{x}\,,1\,]+\left[\hat{x}\,,\left(\frac{-ia\hat{P}}{\hbar}\right)\right]+\left[\hat{x}\,,\left(\frac{-ia\hat{P}}{\hbar}\right)^2\right]+---$$

$$\left[\hat{x}\,,e^{\frac{-ia\hat{P}}{\hbar}}\right]=0-\frac{ia}{\hbar}\left[\hat{x}\,,\hat{P}\,\right]+\left(\frac{ia}{\hbar}\right)^2\left[\hat{x}\,,\hat{P}^2\,\right]+---$$

$$\left[\hat{x}\,,e^{\frac{-ia\hat{P}}{\hbar}}\right]=\frac{-ia}{\hbar}(i\hbar)+\left(\frac{ia}{\hbar}\right)^2\left(ii\hbar\hat{P}\,\right)+---$$

$$\left[\hat{x}\,,e^{\frac{-ia\hat{P}}{\hbar}}\right]=a\left\{1+\frac{\left(-\frac{ia\hat{P}}{\hbar}\right)}{1!}+\frac{\left(-\frac{ia\hat{P}}{\hbar}\right)^2}{2!}+---\right\}$$

$$\Rightarrow\left[\hat{x}\,,e^{\frac{-ia\hat{P}}{\hbar}}\right]=ae^{\frac{-ia\hat{P}}{\hbar}}$$

39. For momentum operator $\hat{P}$, show that $\left[\hat{P}\,,e^{\hat{P}}\,\right]=0$?

Solution

$$\left[\hat{P}\,,e^{\hat{P}}\,\right]=\left[\hat{P}\,,\sum_{n=0}^{\infty}\frac{\hat{P}^n}{n!}\right]=\sum_{n=0}^{\infty}\frac{1}{n!}\left[\hat{P}\,,\hat{P}^n\,\right]=\sum_{n=0}^{\infty}\frac{1}{n!}(0)=0$$

40. Show that the operator $i\left(\hat{P}^2\hat{x}-\hat{x}\hat{P}^2\right)$ is Hermitian?

Solution

Given operator $i\left(\hat{P}^2\hat{x} - \hat{x}\hat{P}^2\right)$

Take Hermitian conjugate

$$\left\{i\left(\hat{P}^2\hat{x} - \hat{x}\hat{P}^2\right)\right\}^\dagger = \left(i\hat{P}^2\hat{x}\right)^\dagger - \left(i\hat{x}\hat{P}^2\right)^\dagger$$

$$\left\{i\left(\hat{P}^2\hat{x} + \hat{x}\hat{P}^2\right)\right\}^\dagger = -i\hat{x}^\dagger\hat{P}^{2\dagger} + i\hat{P}^{2\dagger}\hat{x}^\dagger = i\left(\hat{P}^2\hat{x} - \hat{x}\hat{P}^2\right)$$

So operator $i\left(\hat{P}^2\hat{x} - \hat{x}\hat{P}^2\right)$ is Hermitian.

41. The normalized wave function of a particle in one dimensional box of length L is given by

$\psi = \sqrt{\frac{2}{L}} sin\left(\frac{\pi x}{L}\right)$, find expectation value of momentum of that particle?

Solution

As expectation value is expressed as

$$\langle\hat{P}\rangle = \int_{-\infty}^{\infty} \psi^* \hat{P}\psi dx$$

$$\langle\hat{P}\rangle = \int_{-0}^{L} \sqrt{\frac{2}{L}} sin\left(\frac{\pi x}{L}\right)\left(-i\hbar\frac{\partial}{\partial x}\right)\sqrt{\frac{2}{L}} sin\left(\frac{\pi x}{L}\right) dx$$

$$\langle\hat{P}\rangle = \frac{-2i\hbar}{L}\frac{\pi}{L}\int_{0}^{L} sin\left(\frac{\pi x}{L}\right) cos\left(\frac{\pi x}{L}\right) dx = 0$$

42. Show that the wave function $\psi_n = \sqrt{\frac{2}{L}} sin\left(\frac{n\pi x}{L}\right)$ is orthonormal?

Solution

As orthonormal condition is written as

$$\int_{-\infty}^{+\infty} {\psi_m}^* \psi_n dv = \delta_{mn}$$

δ_{mn} is called kronecker delta. Where $\delta_{mn} = \begin{cases} 0 & if\ m \neq n \\ 1 & if\ m = n \end{cases}$ So

$$\int_0^L \psi_m{}^* \psi_n dx = \int_0^L \sqrt{\frac{2}{L}} sin\left(\frac{m\pi x}{L}\right) \sqrt{\frac{2}{L}} sin\left(\frac{n\pi x}{L}\right) dx$$

$$\int_0^L \psi_m{}^* \psi_n dx = \frac{1}{L}\int_0^L 2\ sin\left(\frac{m\pi x}{L}\right) sin\left(\frac{n\pi x}{L}\right) dx$$

$$\int_0^L \psi_m{}^* \psi_n dx = \frac{1}{L}\int_0^L \left\{\cos\left(\frac{m-n}{L}\right)\pi x - \cos\left(\frac{m+n}{L}\right)\pi x\right\} dx$$

$$\int_0^L \psi_m{}^* \psi_n dx = \frac{1}{L}\left\{\left|\frac{\sin\left(\frac{m-n}{L}\right)\pi x}{\left(\frac{m-n}{L}\right)\pi}\right|_0^{\mathrm{L}} - \left|\frac{\sin\left(\frac{m+n}{L}\right)\pi x}{\left(\frac{m+n}{L}\right)\pi}\right|_0^{\mathrm{L}}\right\} = \begin{cases} 0 & if\ m \neq n \\ 1 & if\ m = n \end{cases}$$

This means wave function is orthonormal.

43. The most general solution of time dependent Schrodinger's equation is expressed as linear combination of the stationary states $\psi(x,0) = \sum_{n=1}^{\infty} c_n \Phi_{\mathrm{n}}(x)$.Where $\Phi_{\mathrm{n}}(\mathrm{x})$ are the orthonormal set of Eigen functions of particle in an infinite square well. Show that $\sum_{n=1}^{\infty} |c_n|^2 = 1$?

Solution

Complete wave function corresponding to Time dependent Schrodinger's equation is

$$\psi(x,t) = \sum_{n=1}^{\infty} c_n \Phi_{\mathrm{n}}(x) e^{\frac{-iEt}{\hbar}}$$

Here stationary states are $\sum_{n=1}^{\infty} c_n \Phi_{\mathrm{n}}(x)$.

Now we normalized the stationary states. Normalized condition is

$$\int_{-\infty}^{+\infty} \psi_m{}^* \psi_n dx = \delta_{mn}$$

$$\int_{-\infty}^{+\infty} \sum_{m=1}^{\infty} c_m{}^* \Phi_m{}^*(x) \sum_{n=1}^{\infty} c_n \Phi_n(x) dx = \delta_{mn}$$

δ_{mn} is called kronecker delta. Where $\delta_{mn} = \begin{cases} 0 & if\ m \neq n \\ 1 & if\ m = n \end{cases}$

For the condition $m = n$ we have

$$\int_{-\infty}^{+\infty} \sum_{n=1}^{\infty} c_n{}^* \Phi_n{}^*(x) \sum_{n=1}^{\infty} c_n \Phi_n(x) dx = 1$$

$$\sum_{n=1}^{\infty} |c_n|^2 \int_{-\infty}^{+\infty} \Phi_n{}^*(x)\, \Phi_n(x) dx = 1$$

$$\Rightarrow \sum_{n=1}^{\infty} |c_n|^2 = 1$$

44. Show that

a. $\left[\hat{x}^{\,2}, \hat{P}_x\right] = 2i\hbar x$

b. $\left[\hat{x}^{\,n}, \hat{P}_x\right] = ni\hbar x$

Solution

a. $\left[\hat{x}^{\,2}, \hat{P}_x\right] = \hat{x}\left[\hat{x}, \hat{P}_x\right] + \left[\hat{x}, \hat{P}_x\right]\hat{x} = \hat{x}i\hbar + i\hbar\hat{x} = 2i\hbar x$

b. $\left[\hat{x}^{\,n}, \hat{P}_x\right] = ni\hbar x$

As $\left[\hat{x}^{\,2}, \hat{P}_x\right] = 2i\hbar x$ similarly

$$\left[\hat{x}^{\,3}, \hat{P}_x\right] = 3i\hbar x$$

$$\left[\hat{x}^{\,4}, \hat{P}_x\right] = 4i\hbar x$$

In general

$$\left[\hat{x}^{\,n}, \hat{P}_x\right] = ni\hbar x$$

In the same way we can show that

c. $\left[\hat{x}, \hat{P}_x{}^{n}\right] = ni\hbar \hat{P}_x{}^{n-1}$

45. Show whether the wave function $\psi = c(1 + x^2)$ is an eigen function of the momentum operator $\hat{P}_x$?

Solution

Now Eigen value equation is

$$\hat{A}\,\psi = a\psi$$

$$\hat{P}\,\psi = \left(-i\hbar\frac{\partial}{\partial x}\right)c(1+x^2) = -2i\hbar cx \neq a\psi$$

So $\psi = c(1+x^2)$ is not an Eigen function of momentum operator $\hat{P}_x$.

46. Prove that $\sin(\theta)$ and $\cos(\theta)$ are orthogonal in the interval$[0,\pi]$?

Solution

Orthogonal condition is

$$\int_0^{\pi} {\psi_m}^*\ \psi_n dx = \int_0^{\pi} \sin(\theta)\ \cos(\theta)\, d\theta = \left|\frac{\sin^2(\theta)}{2}\right|_0^{\pi} = 0$$

This proves, that $\sin(\theta)$ and $\cos(\theta)$ are orthogonal in the interval$[0,\pi]$.

47. Let $\psi = c_0\psi_0 + c_1\psi_1 + c_2\psi_2$ where $\psi_0, \psi_1 and\ \psi_2$ are normalized to unity.Show that ${c_0}^2 + {c_1}^2 + {c_2}^2 = 1$

Solution

As normalized condition is

$$\int_{-\infty}^{\infty} \psi^*\ \psi dx = 1$$

$$\int_{-\infty}^{\infty} \left({c_0}^*{\psi_0}^* + {c_1}^*{\psi_1}^* + {c_2}^*{\psi_2}^*\right)\left(c_0\psi_0 + c_1\psi_1 + c_2\psi_2\right)dx = 1$$

$$\int_{-\infty}^{\infty} \left({c_0}^*{\psi_0}^* c_0\psi_0 + {c_1}^*{\psi_1}^* c_1\psi_1 + {c_2}^*{\psi_2}^* c_2\psi_2\right)dx = 1$$

$$\int_{-\infty}^{\infty} \left({c_0}^2{\psi_0}^*\psi_0 + {c_1}^2{\psi_1}^*\psi_1 + {c_2}^2{\psi_2}^*\psi_2\right)dx = 1$$

$$\int_{-\infty}^{\infty} \left(c_0{}^2\psi_0{}^*\psi_0 + c_1{}^2\psi_1{}^*\psi_1 + c_2{}^2\psi_2{}^*\psi_2\right) dx = 1$$

$$\Rightarrow c_0{}^2 + c_1{}^2 + c_2{}^2 = 1$$

48. Consider the normalized wave function $\psi = \sqrt{\frac{a}{\pi}} e^{-\frac{a(x-x_o)^2}{2}}$. Find expectation value of position operator $\hat{x}$?

Solution

As Expectation value is

$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} \psi^* \hat{x} \psi dx$$

$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} \sqrt{\frac{a}{\pi}} e^{-\frac{a(x-x_o)^2}{2}} \hat{x} \sqrt{\frac{a}{\pi}} e^{-\frac{a(x-x_o)^2}{2}} dx = \frac{a}{\pi} \int_{-\infty}^{\infty} \hat{x} e^{-\frac{2a(x-x_o)^2}{2}} dx$$

Put $x - x_o = u$ $\Rightarrow dx = du$ So

$$\langle \hat{x} \rangle = \frac{a}{\pi} \int_{-\infty}^{\infty} (u + x_o) e^{-\frac{2au^2}{2}} d$$

$$\langle \hat{x} \rangle = \frac{a}{\pi} \int_{-\infty}^{\infty} u e^{-\frac{2au^2}{2}} du + \frac{a}{\pi} \int_{-\infty}^{\infty} x_o e^{-\frac{2au^2}{2}} du = 0 + \frac{a}{\pi} x_o \sqrt{\frac{\pi}{a}} = \sqrt{\frac{a}{\pi}} x_o$$

49. A particle of mass m is in a state $\psi = \left(\frac{2am}{\hbar}\right)^{\frac{1}{4}} e^{-a\left(\frac{mx^2}{\hbar} + it\right)}$, verify $\Delta x \Delta P \geq \frac{\hbar}{2}$?

Solution

We know

$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} \psi^* \hat{x} \psi dx = \int_{-\infty}^{\infty} \left(\frac{2am}{\hbar}\right)^{\frac{1}{4}} e^{-a\left(\frac{mx^2}{\hbar} - it\right)} \hat{x} \left(\frac{2am}{\hbar}\right)^{\frac{1}{4}} e^{-a\left(\frac{mx^2}{\hbar} + it\right)} dx$$

$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} \left(\frac{2am}{\hbar}\right)^{\frac{1}{2}} \hat{x} e^{-2a\left(\frac{mx^2}{\hbar}\right)} dx = 0$$

Now

$$\langle \hat{x}^2 \rangle = \int_{-\infty}^{\infty} \left(\frac{2am}{\hbar}\right)^{\frac{1}{4}} e^{-a\left(\frac{mx^2}{\hbar} - it\right)} \hat{x}^2 \left(\frac{2am}{\hbar}\right)^{\frac{1}{4}} e^{-a\left(\frac{mx^2}{\hbar} + it\right)} dx = \int_{-\infty}^{\infty} \left(\frac{2am}{\hbar}\right)^{\frac{1}{2}} \hat{x}^2 e^{-2a\left(\frac{mx^2}{\hbar}\right)} dx = \frac{\hbar}{4am}$$

Now expectation value of momentum

$$\langle \hat{P} \rangle = \int_{-\infty}^{\infty} \psi^* \hat{P} \psi dx = \int_{-\infty}^{\infty} \left(\frac{2am}{\hbar}\right)^{\frac{1}{4}} e^{-a\left(\frac{mx^2}{\hbar} - it\right)} \left(-i\hbar \frac{\partial}{\partial x}\right) \left(\frac{2am}{\hbar}\right)^{\frac{1}{4}} e^{-a\left(\frac{mx^2}{\hbar} + it\right)} dx$$

$$\langle \hat{P} \rangle = -i\hbar \left(\frac{2am}{\hbar}\right)^{\frac{1}{2}} \left(\frac{-2am}{\hbar}\right) \int_{-\infty}^{\infty} x e^{-2a\left(\frac{mx^2}{\hbar}\right)} dx = 0$$

Now

$$\langle \hat{P}^2 \rangle = \int_{-\infty}^{\infty} \left(\frac{2am}{\hbar}\right)^{\frac{1}{4}} e^{-a\left(\frac{mx^2}{\hbar} - it\right)} \hat{P}^2 \left(\frac{2am}{\hbar}\right)^{\frac{1}{4}} e^{-a\left(\frac{mx^2}{\hbar} + it\right)} dx = \int_{-\infty}^{\infty} \left(\frac{2am}{\hbar}\right)^{\frac{1}{4}} e^{-a\left(\frac{mx^2}{\hbar} - it\right)} \left(-\hbar^2 \frac{\partial^2}{\partial x^2}\right) \left(\frac{2am}{\hbar}\right)^{\frac{1}{4}} e^{-a\left(\frac{mx^2}{\hbar} + it\right)} dx$$

$$\langle \hat{P}^2 \rangle = -\hbar^2 \left(\frac{2am}{\hbar}\right)^{\frac{1}{2}} \left(\frac{-2am}{\hbar}\right) \int_{-\infty}^{\infty} \left(\frac{\partial}{\partial x}\right) \int_{-\infty}^{\infty} x e^{-2a\left(\frac{mx^2}{\hbar}\right)} dx = am\hbar$$

Now

$$\Delta x \Delta P = \sqrt{\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2} \sqrt{\langle \hat{P}^2 \rangle - \langle \hat{P} \rangle^2} = \sqrt{\frac{\hbar}{4am} - 0} \times \sqrt{am\hbar - 0}$$

$$\Delta x \Delta P = \frac{\hbar}{2}$$

50. Normalized wave function for a one dimensional box is given by $\psi = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$.

verify $\Delta x \Delta P \geq \frac{\hbar}{2}$?

Solution

We know

$$\langle \hat{x} \rangle = \int_0^L \psi^* \, \hat{x} \psi dx = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \hat{x} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx$$

$$\langle \hat{x} \rangle = \frac{2}{L} \int_0^L \hat{x} \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{2}{L} \int_0^L \hat{x} \left(\frac{1 - \cos\left(\frac{2n\pi x}{L}\right)}{2} \right) dx$$

$$\langle \hat{x} \rangle = \frac{1}{L} \int_0^L \hat{x} \, dx - \frac{1}{L} \int_0^L \hat{x} \cos\left(\frac{2n\pi x}{L}\right) dx = \frac{1}{L} \left| \frac{x^2}{2} \right|_0^L - 0 = \frac{1}{L} \times \frac{L^2}{2} = \frac{L}{2}$$

Now

$$\langle \hat{x}^2 \rangle = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \hat{x}^2 \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx = \frac{2}{L} \int_0^L \hat{x}^2 \left(\frac{1 - \cos\left(\frac{2n\pi x}{L}\right)}{2} \right) dx$$

$$\langle \hat{x}^2 \rangle = \frac{1}{L} \int_0^L \hat{x}^2 \, dx - \frac{1}{L} \int_0^L \hat{x}^2 \cos\left(\frac{2n\pi x}{L}\right) dx = L^2 \left(\frac{1}{3} - \frac{1}{2n^2\pi^2} \right)$$

Now expectation value of momentum

$$\langle \hat{P} \rangle = \int_{-\infty}^{\infty} \psi^* \, \hat{P} \psi dx = \int_{-\infty}^{\infty} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \left(-i\hbar \frac{\partial}{\partial x}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx$$

$$\langle \hat{P} \rangle = -i\hbar \frac{2}{L} \left(\frac{n\pi}{L}\right) \int_{-\infty}^{\infty} \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) dx = 0$$

Now

$$\langle \hat{P}^2 \rangle = \int_{-\infty}^{\infty} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \hat{P}^2 \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx = \int_{-\infty}^{\infty} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \left(-\hbar^2 \frac{\partial^2}{\partial x^2}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx$$

$$\langle \hat{P}^2 \rangle = \frac{n^2\pi^2\hbar^2}{L^2}$$

Now

$$\Delta x \Delta P = \sqrt{\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2}\sqrt{\langle \hat{P}^2 \rangle - \langle \hat{P} \rangle^2} = \sqrt{L^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right) - \frac{L^2}{4}} \times \sqrt{\frac{n^2\pi^2\hbar^2}{L^2} - 0}$$

$$\Delta x \Delta P = \hbar\sqrt{\left(\frac{n^2\pi^2}{12} - \frac{n^2\pi^2}{2n^2\pi^2}\right)} = \hbar\sqrt{\left(\frac{n^2\pi^2}{12} - \frac{1}{2}\right)} \geq \frac{\hbar}{2}$$

51. A particle in the infinite square well has initial wave function is

$\psi(x,0) = A\sin^3\left(\frac{\pi x}{L}\right)$. Find normalized $\psi(x,t)$?

Solution

As $\sin 3\alpha = 3sin\alpha - 4sin^3$ So $sin^3\alpha = \frac{3}{4}sin\alpha - \frac{1}{4}\sin 3\alpha$

$$\Rightarrow \psi(x,0) = \frac{3A}{4}sin\left(\frac{\pi x}{L}\right) - \frac{A}{4}\sin 3\left(\frac{\pi x}{L}\right)$$

$$\Rightarrow \psi(x,0) = \frac{3A}{4}\sqrt{\frac{2}{L}}\sqrt{\frac{L}{2}}sin\left(\frac{\pi x}{L}\right) - \frac{A}{4}\sqrt{\frac{2}{L}}\sqrt{\frac{L}{2}}\sin 3\left(\frac{\pi x}{L}\right)$$

$$\Rightarrow \psi(x,0) = A\sqrt{\frac{L}{2}}\left(\frac{3}{4}\sqrt{\frac{2}{L}}sin\left(\frac{\pi x}{L}\right)\right) - A\sqrt{\frac{L}{2}}\left(\frac{1}{4}\sqrt{\frac{2}{L}}sin\left(\frac{\pi x}{L}\right)\right) =$$

As $\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ So

$$\psi(x,0) = A\sqrt{\frac{L}{2}}\left(\frac{3}{4}\psi_1 - \frac{1}{4}\psi_3\right)$$

Now Normalized wave function will be

$$\int_0^L \psi^*(x,0)\psi(x,0)dx = 1$$

$$\int_0^L \left\{A\sqrt{\frac{L}{2}}\left(\frac{3}{4}\psi_1 - \frac{1}{4}\psi_3\right)\right\}\left\{A\sqrt{\frac{L}{2}}\left(\frac{3}{4}\psi_1 - \frac{1}{4}\psi_3\right)\right\}dx = 1$$

$$\frac{A^2L}{2}\int_0^L \left(\frac{3}{4}\psi_1 - \frac{1}{4}\psi_3\right)\left(\frac{3}{4}\psi_1 - \frac{1}{4}\psi_3\right)dx = 1$$

$$\frac{A^2L}{2}\int_0^L \left(\frac{3}{4}\psi_1 \times \frac{3}{4}\psi_1 - \frac{1}{4}\psi_3 \times \frac{3}{4}\psi_1 - \frac{3}{4}\psi_1 \times \frac{1}{4}\psi_3 + \frac{1}{4}\psi_3 \times \frac{1}{4}\psi_3\right)dx = 1$$

$$\frac{A^2L}{2}\left(\frac{9}{16} - 0 - 0 + \frac{1}{16}\right) = 1 \Rightarrow \frac{10A^2L}{32} = 1$$

$$\Rightarrow A = \sqrt{\frac{32}{10L}}$$

Normalized wave function will be

$$\psi(x,0) = \sqrt{\frac{32}{10L}}\sin^3\left(\frac{\pi x}{L}\right)$$

Or

$$\psi(x,0) = \sqrt{\frac{32}{10L}}\sqrt{\frac{L}{2}}\left(\frac{3}{4}\psi_1 - \frac{1}{4}\psi_3\right) = \sqrt{\frac{1}{10}}(3\psi_1 - \psi_3)$$

And $$\psi(x,t) = \sqrt{\frac{1}{10}}\left(3\psi_1 e^{\frac{-iE_1 t}{\hbar}} - \psi_3 e^{\frac{-iE_3 t}{\hbar}}\right)$$

And $$|\psi(x,t)|^2 = \frac{1}{10}\left(9{\psi_1}^2 + {\psi_3}^2 - 6\psi_1\psi_3\, cos\left(\frac{E_3 - E_1}{\hbar}\right)t\right)$$

52. Consider Hamiltonian of a system is $\widehat{H} = \frac{P^2}{2m} + V$. Evaluate

a. $\left[\hat{H},\hat{x}\right]$ and b. $\langle\hat{P}\rangle$

Solution

a. $\left[\hat{H},\hat{x}\right]=\left[\frac{P^2}{2m}+V,\hat{x}\right]=\left[\frac{P^2}{2m},\hat{x}\right]+[V,\hat{x}]$

$$\left[\hat{H},\hat{x}\right]=\frac{P^2}{2m}\hat{x}-\hat{x}\frac{P^2}{2m}+V\hat{x}-\hat{x}V=\frac{1}{2m}(P^2\hat{x}-\hat{x}P^2)$$

$$\Rightarrow\left[\hat{H},\hat{x}\right]=\frac{1}{2m}[P^2,\hat{x}]=\frac{1}{2m}(-2i\hbar P)=\frac{-i\hbar P}{m}$$

b. $\langle\hat{P}\rangle$

As

$$\left[\hat{H},\hat{x}\right]=\frac{-i\hbar P}{m}$$

$$\hat{P}=\frac{-m}{i\hbar}\left[\hat{H},\hat{x}\right]=\frac{-m}{i\hbar}\left(\hat{H}\hat{x}-\hat{x}\hat{H}\right)$$

Now

$$\langle\hat{P}\rangle=\int_{-\infty}^{\infty}\psi^*\hat{P}\psi dx=\frac{-m}{i\hbar}\int_{-\infty}^{\infty}\psi^*\left(\hat{H}\hat{x}-\hat{x}\hat{H}\right)\psi dx$$

$$\langle\hat{P}\rangle=\frac{-m}{i\hbar}\int_{-\infty}^{\infty}\left(\psi^*\hat{H}\hat{x}\psi-\psi^*\hat{x}\hat{H}\psi\right)dx$$

As $\hat{H}\psi=a\psi$ and$\left(\hat{H}\psi\right)^*=\psi^*\hat{H}^\dagger=\psi^*\hat{H}=a^*\psi^*=a\psi^*=\psi^*a.$ as Eigen value of Hermitian operator is real. So,

$$\Rightarrow\langle\hat{P}\rangle=\frac{-m}{i\hbar}\int_{-\infty}^{\infty}(\psi^*a\hat{x}\psi-\psi^*\hat{x}a\psi)\,dx=0$$

53. Consider a particle in a state$\psi=Ae^{-\frac{(x-x_O)^2}{4a^2}}e^{\frac{iP_Ox}{\hbar}}e^{-i\omega_Ot}$. Calculate uncertainty ΔP?

Solution

As

$$\langle \hat{P} \rangle = \int_{-\infty}^{\infty} \psi^* \, \hat{P} \psi dx = \int_{-\infty}^{\infty} A e^{-\frac{(x-x_O)^2}{4a^2}} e^{\frac{-iP_O x}{\hbar}} e^{+i\omega_o t} \left(-i\hbar \frac{\partial}{\partial x}\right) A e^{-\frac{(x-x_O)^2}{4a^2}} e^{\frac{iP_O x}{\hbar}} e^{-i\omega_o t} dx$$

$$\langle \hat{P} \rangle = -i\hbar |A|^2 \int_{-\infty}^{\infty} e^{-\frac{(x-x_O)^2}{4a^2}} e^{\frac{-iP_O x}{\hbar}} \left\{ \left(\frac{-2x}{4a^2}\right) e^{-\frac{(x-x_O)^2}{4a^2}} e^{\frac{iP_O x}{\hbar}} + \left(\frac{iP_o}{\hbar}\right) e^{-\frac{(x-x_O)^2}{4a^2}} e^{\frac{iP_O x}{\hbar}} \right\} dx$$

$$\langle \hat{P} \rangle = -i\hbar |A|^2 \left\{ \left(\frac{-1}{2a^2}\right) \int_{-\infty}^{\infty} x e^{-\frac{2(x-x_O)^2}{4a^2}} dx + \left(\frac{iP_o}{\hbar}\right) \int_{-\infty}^{\infty} e^{-\frac{2(x-x_O)^2}{4a^2}} dx \right\}$$

$$\langle \hat{P} \rangle = P_o$$

Now

$$\langle \hat{P}^2 \rangle = A e^{-\frac{(x-x_O)^2}{4a^2}} e^{\frac{-iP_O x}{\hbar}} e^{+i\omega_o t} \hat{P}^2 A e^{-\frac{(x-x_O)^2}{4a^2}} e^{\frac{iP_O x}{\hbar}} e^{-i\omega_o t} dx$$

$$\langle \hat{P}^2 \rangle = A e^{-\frac{(x-x_O)^2}{4a^2}} e^{\frac{-iP_O x}{\hbar}} e^{+i\omega_o t} \left(-\hbar^2 \frac{\partial^2}{\partial x^2}\right) A e^{-\frac{(x-x_O)^2}{4a^2}} e^{\frac{iP_O x}{\hbar}} e^{-i\omega_o t} dx$$

$$\langle \hat{P}^2 \rangle = {P_o}^2 + \frac{\hbar^2}{4a^2}$$

Now

$$\Delta P = \sqrt{\langle \hat{P}^2 \rangle - \langle \hat{P} \rangle^2} = \sqrt{{P_o}^2 + \frac{\hbar^2}{4a^2} - {P_o}^2} = \frac{\hbar}{2a}$$

54. Find the time evolution of the following wave functions

a. $\psi_1 = A \sin \omega t \cos k(x + ct)$

b. $\psi_2 = A \sin(10^{-5}\, k(x - ct) \cos k(x - ct)$

Solution

a. $\psi_1 = A \sin \omega t \cos k(x + ct)$

After time Δt,

$$\psi_1 = A \sin \omega(t + \Delta t) \cos k(x - c\Delta t + c(t + \Delta t)) = A\{\sin \omega(t + \Delta t) \cos k(x + ct)\}$$

$$\psi_1 = A\{\sin \omega t \cos \omega \Delta t + \cos \omega t \sin \omega \Delta t\} \cos k(x + ct)$$

IfΔt is small then $\cos\omega\Delta t = 1$ and $\sin\omega\Delta t = \omega\Delta t$ so,

$$\psi_1 = A\{\sin\omega t + \omega\Delta t\cos\omega t\}\cos k(x+ct)$$

Part b will same as part a.

55. For one dimensional box problem, show that probability density is maximum at the value $x = x_i$ such that $x_i = \left(\frac{2i+1}{2n}\right)L$. Her L is the length of the box.?

Solution

As wave function of a particle in one dimensional box is given by the equation

$$\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

Now the probability density P is

$$P = \psi^*\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) = \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)$$

Now the Probability will be maximum when

$$\sin^2\left(\frac{n\pi x}{L}\right) = 1 \Rightarrow \sin\left(\frac{n\pi x}{L}\right) = \pm 1$$

$$\Rightarrow \frac{n\pi x_i}{L} = \sin^{-1}\pm 1 = (2i+1)\frac{\pi}{2}$$

$$\Rightarrow x_i = (2i+1)\frac{\pi}{2}\frac{L}{n\pi} = \left(\frac{2i+1}{2n}\right)L$$

56. Wave function for a free particle moving in one dimension is given by

$$\psi = Ae^{ikx} + \frac{A}{\sqrt{2}}e^{-ikx}$$

Find the Eigen value of momentum also?

Solution

As Eigen value equation is

$$\hat{A}\,\psi = a\psi$$

$$\hat{P}\,\psi = \left(-i\hbar\frac{\partial}{\partial x}\right)\left(Ae^{ikx} + \frac{A}{\sqrt{2}}e^{-ikx}\right) = -i\hbar Aike^{ikx} - i\hbar\frac{A}{\sqrt{2}}(-ik)e^{-ikx}$$

$$\hat{P}\,\psi = \hbar Ake^{ikx} + \hbar k\frac{A}{\sqrt{2}}e^{-ikx} = \hbar k\left(Ae^{ikx} + \frac{A}{\sqrt{2}}e^{-ikx}\right)$$

So eigen value of momentum corresponding to above wave function is $\hbar k$.

57. Find $\langle\hat{x}\,\rangle$ and Δx for the following probability densities?

    a. $P = Ax^2e^{\frac{-x^2}{2a^2}}$

    b. $P = \frac{A}{a^4+(x-x_o)^2}$

Solution

a. As $\langle\hat{x}\,\rangle = \int_{-\infty}^{\infty}\psi^*\,\hat{x}\psi dx = \int_{-\infty}^{\infty}\hat{x}\psi^*\,\psi dx = \int_{-\infty}^{\infty}\hat{x}\,|\psi|^2dx = \int_{-\infty}^{\infty}\hat{x}\,Pdx$

$$\langle\hat{x}\,\rangle = \int_{-\infty}^{\infty}\hat{x}\left(Ax^2e^{\frac{-x^2}{2a^2}}\right)dx = 0$$

Now $\langle\hat{x}^{\,2}\rangle = \int_{-\infty}^{\infty}\hat{x}^2\left(Ax^2e^{\frac{-x^2}{2a^2}}\right)dx = A\int_{-\infty}^{\infty}x^4e^{\frac{-x^2}{2a^2}}\,dx = 2a^2$

Now $\Delta x = \sqrt{\langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2} = \sqrt{2a^2-0} = \sqrt{2}a$

58. Wave function of a particle moving in one dimension is $\psi = Ae^{i(ax-bt)}$

    Find potential V(x) in which particle is moving. What will be the momentum of that particle?

Solution

As Schrödinger's time dependent equation is

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi$$

$$i\hbar\frac{\partial}{\partial t}\left(Ae^{i(ax-bt)}\right) = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(Ae^{i(ax-bt)}\right) + V\left(Ae^{i(ax-bt)}\right)$$

$$i(-ib)\hbar Ae^{i(ax-bt)} = \frac{-\hbar^2}{2m}(ia)^2 Ae^{i(ax-bt)} + VAe^{i(ax-bt)}$$

$$V = b\hbar - \frac{a^2\hbar^2}{2m}$$

Now $$\hat{P}\psi = -i\hbar\frac{\partial}{\partial x}\left(Ae^{i(ax-bt)}\right) = -i\hbar(ia)\left(Ae^{i(ax-bt)}\right) = a\hbar\psi$$

$$\hat{P} = a\hbar$$

Corresponding energy will be

$$\hat{E}\psi = i\hbar\frac{\partial}{\partial t}\left(Ae^{i(ax-bt)}\right) = i\hbar(-ib)\left(Ae^{i(ax-bt)}\right) = b\hbar\psi$$

59. The wave function of a particle moving along x-axis is given by $\psi = Ae^{i(kx-\omega t)}$. Find potential V?

Solution

As Schrödinger's time dependent equation is

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi$$

$$i\hbar\frac{\partial}{\partial t}\left(Ae^{i(kx-\omega t)}\right) = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(Ae^{i(kx-\omega t)}\right) + V\left(Ae^{i(kx-\omega t)}\right)$$

$$i(-i\omega)\hbar Ae^{i(ax-bt)} = \frac{-\hbar^2}{2m}(ik)^2 Ae^{i(ax-bt)} + VAe^{i(ax-bt)}$$

$$V = \omega\hbar - \frac{k^2\hbar^2}{2m}$$

60. The probability wave function of a moving particle is given by the equation $|\psi|^2 = Ae^{-a(x-b)^2}$. Normalize this wave function and find uncertainty Δx in its position?

Solution

Normalized condition is

$$\int_0^L \psi^* \psi dx = 1$$

$$\int_0^L |\psi|^2 dx = 1 \Rightarrow \int_0^L A e^{-a(x-b)^2} dx = 1 \Rightarrow A = \sqrt{\frac{a}{\pi}}$$

Now

$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} \psi^* \hat{x} \psi dx = \int_{-\infty}^{\infty} \hat{x} \psi^* \psi dx = \int_{-\infty}^{\infty} \hat{x} |\psi|^2 dx = \int_{-\infty}^{\infty} \hat{x} A e^{-a(x-b)^2} dx = b$$

$$\langle \hat{x}^2 \rangle = \int_{-\infty}^{\infty} \hat{x}^2 \left(A e^{-a(x-b)^2} \right) dx = b^2 + \frac{1}{a^2}$$

$$\Delta x = \sqrt{b^2 + \frac{1}{a^2} - b^2} = \frac{1}{a}$$

61. Let $/\psi\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$ and $/\Phi\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$, Show that whether these state vectors are orthogonal or not. Is $/\psi\rangle$ normalized?

Solution

If $/\psi\rangle$ and $/\Phi\rangle$ are orthogonal then $\langle \psi | \Phi \rangle = 0$. Now

$$\langle \psi | \Phi \rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix} = \frac{1}{2} - \frac{1}{2} = 0$$

So, $/\psi\rangle$ and $/\Phi\rangle$ are orthogonal.

Now we check whether $/\psi\rangle$ is normalized or not. Normalization condition is

$$\langle \psi | \psi \rangle = 1$$

Now $$\langle \psi | \psi \rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \frac{1}{2} + \frac{1}{2} = 1$$

Hence $/\psi\rangle$ is normalized.

62. Let $/\psi\rangle = \begin{pmatrix} 2 \\ -7i \\ 1 \end{pmatrix}$ and $/\Phi\rangle = \begin{pmatrix} 1+3i \\ 4 \\ 8 \end{pmatrix}$ find $\langle\psi|\Phi\rangle$ and $\langle\Phi|\psi\rangle$?

Solution

$$\langle\psi|\Phi\rangle = \begin{pmatrix} 2 & 7i & 1 \end{pmatrix}\begin{pmatrix} 1+3i \\ 4 \\ 8 \end{pmatrix} = 2+6i+28i+8 = 10+34i$$

Now

$$\langle\Phi|\psi\rangle = \begin{pmatrix} 1-3i & 4 & 8 \end{pmatrix}\begin{pmatrix} 2 \\ -7i \\ 1 \end{pmatrix} = 2-6i-28i+8 = 10-34i$$

63. Consider a vector $/\psi\rangle = \begin{pmatrix} x \\ 3x \\ -2x \end{pmatrix}$, find value of x such that $/\psi\rangle$ is normalized.?

Solution

When $/\psi\rangle$ is normalized then

$$\langle\psi|\psi\rangle = 1$$

$$\Rightarrow \begin{pmatrix} x & 3x & -2x \end{pmatrix}\begin{pmatrix} x \\ 3x \\ -2x \end{pmatrix} = 1 \Rightarrow x^2+9x^2+4x^2 = 1$$

$$\Rightarrow 14x^2 = 1 \Rightarrow x = \pm\frac{1}{\sqrt{14}}$$

64. Which of the following sets of linearly independent?

a. $\{(3,0,0),(0,-2,0),(0,0,-1)\}$

b. $\{(6,-9,0),(-2,3,0)\}$

Solution

a. Consider scalars a,b and c such that

$$a(3,0,0)+b(0,-2,0)+c(0,0,-1) = 0$$
$$\Rightarrow (3a,0,0)+(0,-2b,0)+(0,0,-c) = 0$$
$$\Rightarrow (3a,-2b,-c) = 0 \Rightarrow 3a = 0, -2b = 0, -c = 0$$

$$\Rightarrow a = 0, b = 0, c = 0$$

So given set of vectors is linearly independent.

b. $\{(6, -9,0), (-2,3,0)\}$

In this set vector $(-2,3,0)$ can be written as

$$(-2,3,0) = \frac{1}{-3}(6, -9,0)$$

This shows one of the vector can be expressed as linear combination of other. So this given set of vectors is linearly dependent.

65. Let an operator $\hat{A} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ find corresponding Eigen values and Eigen function?

Solution

As Eigen value equation is

$$\hat{A}/\psi\rangle = \lambda/\psi\rangle$$

Here $/\psi\rangle$ is Eigen vector and λ is Eigen value. We can write above equation as

$$\hat{A}/\psi\rangle = \lambda I/\psi\rangle$$

Here $I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ an identity matrix.

$$\left(\hat{A} - \lambda I\rangle\right)/\psi\rangle = 0$$

Since $/\psi\rangle \neq 0$ so, $\left(\hat{A} - \lambda I\right)$ is non- singular. This means that

$$det\left(\hat{A} - \lambda I\right) = 0$$

$$\Rightarrow \left|\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \lambda \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right| = 0$$

$$\Rightarrow \begin{vmatrix} 1-\lambda & 0 \\ 0 & -1-\lambda \end{vmatrix} = 0$$

$$\Rightarrow (1-\lambda)(-1-\lambda) = 0 \Rightarrow \lambda = 1, -1$$

When $\lambda = 1$ we have $\hat{A} - \lambda I = \begin{pmatrix} 1 & 0 \\ 0 & -2 \end{pmatrix} \tilde{R} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} by \frac{-1}{2} R_2$

$$\Rightarrow x_2 = 0 \Rightarrow \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} x_1 \\ 0 \end{pmatrix} = x_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

So, Eigen vector related to Eigen value $\lambda = 1$, $/\psi_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

Now when $\lambda = -1$ we have $\hat{A} - \lambda I = \begin{pmatrix} -2 & 0 \\ 0 & 0 \end{pmatrix} \tilde{R} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} by \frac{-1}{2} R_1$

$$\Rightarrow x_1 = 0 \Rightarrow \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} 0 \\ x_2 \end{pmatrix} = x_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

So, Eigen vector related to Eigen value $\lambda = -1$, $/\psi_2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

66. Show that $\left(\hat{A}\hat{B}\right)^{\dagger} = \hat{B}^{\dagger}\hat{A}^{\dagger}$

Solution

Consider two arbitrary Eigen functions $/\psi\rangle$ and $/\Phi\rangle$, Then

$$\langle\psi|\left(\hat{A}\hat{B}\right)|\Phi\rangle^{*} = \left\langle\psi\middle|\left(\hat{A}\hat{B}\right)^{\dagger}\middle|\Phi\right\rangle$$

$$\Rightarrow \left\langle\Phi\middle|\left(\hat{A}\hat{B}\right)^{\dagger}\middle|\psi\right\rangle = \langle\psi|\left(\hat{A}\hat{B}\right)|\Phi\rangle^{*}$$

$$\Rightarrow \left\langle\Phi\middle|\left(\hat{A}\hat{B}\right)^{\dagger}\middle|\psi\right\rangle = \langle\psi|\hat{A}|\chi\rangle^{*} \; where \; \hat{B}/\Phi\rangle = /\chi\rangle \; then \left(\hat{B}/\Phi\rangle\right)^{*} = < \Phi/\hat{B}^{\dagger}\rangle =< \chi/$$

$$\Rightarrow \left\langle\Phi\middle|\left(\hat{A}\hat{B}\right)^{\dagger}\middle|\psi\right\rangle = \langle\chi|\hat{A}^{\dagger}|\psi\rangle$$

$$\Rightarrow \left\langle\Phi\middle|\left(\hat{A}\hat{B}\right)^{\dagger}\middle|\psi\right\rangle = \langle\Phi|\hat{B}^{\dagger}\hat{A}^{\dagger}|\psi\rangle$$

$$\Rightarrow \left(\hat{A}\hat{B}\right)^{\dagger} = \hat{B}^{\dagger}\hat{A}^{\dagger}$$

67. Consider two operators $\hat{A}$ and $\hat{A}$ such that $\left[\hat{A}, \hat{A}\right] = i\hat{C}$, Then show that product of the uncertainties $\Delta\hat{A}\Delta\hat{B} \geq \frac{1}{2}\langle\hat{C}\rangle$?

Solution

We know that uncertainty $\Delta\hat{A}^2 = \langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2$

Let $\hat{E} = \hat{A} - \langle\hat{A}\rangle$ and $\hat{F} = \hat{B} - \langle\hat{B}\rangle$

If $/\psi\rangle$ is a wave function then

$$/\psi\rangle = \left(\hat{E} + i\lambda\hat{F}\right)/\psi\rangle$$

Then

$$\langle\psi|\psi\rangle \geq 0$$

$$\Rightarrow \langle\psi|\left(\hat{E} - i\lambda\hat{F}\right)\left(\hat{E} + i\lambda\hat{F}\right)|\psi\rangle \geq 0$$

$$\Rightarrow \left\langle\psi\right|\left(\hat{E}^2 + \lambda^2\hat{F}^2 + i\lambda\left(\hat{E}\hat{F} - \hat{F}\hat{E}\right)\right)\left|\psi\right\rangle \geq 0$$

$$\Rightarrow \left\langle\psi\right|\left(\left(\hat{A} - \langle\hat{A}\rangle\right)^2 + \lambda^2\left(\hat{B} - \langle\hat{B}\rangle\right)^2 + i\lambda\left[\hat{E}, \hat{F}\right]\right)\left|\psi\right\rangle \geq 0$$

$$\Rightarrow \left\langle\psi\right|\left(\left(\hat{A} - \langle\hat{A}\rangle\right)^2 + \lambda^2\left(\hat{B} - \langle\hat{B}\rangle\right)^2 + i\lambda\left[\left(\hat{A} - \langle\hat{A}\rangle\right), \left(\hat{B} - \langle\hat{B}\rangle\right)\right]\right)\left|\psi\right\rangle \geq 0$$

$$\Rightarrow \left\langle\psi\right|\left(\Delta\hat{A}^2 + \lambda^2\Delta\hat{B}^2 + i\lambda[\hat{A}, \hat{B}]\right)\left|\psi\right\rangle \geq 0 \text{------ (1)}$$

This equation will minimum, when

$$\frac{d}{d\lambda}\left\langle\psi\right|\left(\Delta\hat{A}^2 + \lambda^2\Delta\hat{B}^2 + i\lambda[\hat{A}, \hat{B}]\right)\left|\psi\right\rangle = 0$$

$$\Rightarrow \langle\psi|\left(0 + 2\lambda\Delta\hat{B}^2 + i[\hat{A}, \hat{B}]\right)|\psi\rangle = 0$$

$$\Rightarrow \langle\psi|\left(2\lambda\Delta\hat{B}^2\right)|\psi\rangle = -i\langle\psi|\left([\hat{A}, \hat{B}]\right)|\psi\rangle$$

$$\Rightarrow \lambda = -\frac{i\langle\psi|\left([\hat{A}, \hat{B}]\right)|\psi\rangle}{\langle\psi|\left(2\Delta\hat{B}^2\right)|\psi\rangle}$$

Put value of λ in equation 1

$$\Rightarrow \left\langle\psi\right|\left(\Delta\hat{A}^2 + \left(-\frac{i\langle\psi|([\hat{A}, \hat{B}])|\psi\rangle}{\left\langle\psi\right|\left(2\Delta\hat{B}^2\right)\left|\psi\right\rangle}\right)^2 \Delta\hat{B}^2 + i\left(-\frac{i\langle\psi|([\hat{A}, \hat{B}])|\psi\rangle}{\left\langle\psi\right|\left(2\Delta\hat{B}^2\right)\left|\psi\right\rangle}\right)[\hat{A}, \hat{B}]\right)\left|\psi\right\rangle \geq 0$$

$$\Rightarrow \Delta\hat{A}^2 - \frac{\left|\langle\psi|([\hat{A},\hat{B}])|\psi\rangle\right|^2}{4\Delta\hat{B}^4}\Delta\hat{B}^2 + \frac{\left|\langle\psi|([\hat{A},\hat{B}])|\psi\rangle\right|^2}{2\Delta\hat{B}^2} \geq 0$$

$$\Rightarrow \Delta\hat{A}^2 + \frac{\left|\langle\psi|([\hat{A},\hat{B}])|\psi\rangle\right|^2}{4\Delta\hat{B}^2} \geq 0$$

$$\Rightarrow \Delta\hat{A}^2 \geq -\frac{\left|\langle\psi|([\hat{A},\hat{B}])|\psi\rangle\right|^2}{4\Delta\hat{B}^2}$$

$$\Rightarrow \Delta\hat{A}^2\Delta\hat{B}^2 \geq -\frac{\left|\langle\psi|(i\hat{C})|\psi\rangle\right|^2}{4}$$

$$\Rightarrow \Delta\hat{A}^2\Delta\hat{B}^2 \geq \frac{1}{4}\left|\langle\hat{C}\rangle\right|^2$$

$$\Rightarrow \Delta\hat{A}\Delta\hat{B} \geq \frac{1}{2}\langle\hat{C}\rangle$$

68. Show that projection operator is Hermitian?

Solution

Let we have two state vectors $/\psi_1\rangle$ and $/\psi_2\rangle$ and $\hat{P}$ is projection operator then

$$\langle\psi_1|\hat{P}|\psi_2\rangle = \langle\psi_1|\psi_k\rangle\langle\psi_k|\psi_2\rangle = \langle\psi_2|\psi_k\rangle^*\langle\psi_k|\psi_1\rangle^*$$

$$\Rightarrow \langle\psi_1|\hat{P}|\psi_2\rangle = \langle\psi_2|\hat{P}|\psi_1\rangle^*$$

This shows projection operator is Hermitian.

69. For the projection operator$\hat{P}$, show that $\hat{P}^2 = \hat{P}$?

Solution

We can write

$$\hat{P}^2/\psi\rangle = \hat{P}\hat{P}/\psi\rangle = \hat{P}/\psi_i\rangle\langle\psi_i||\psi\rangle$$

$$\Rightarrow \hat{P}^2/\psi\rangle = \hat{P}\hat{P}/\psi\rangle = /\psi_i\rangle\langle\psi_i|\psi_i\rangle\langle\psi_i||\psi\rangle$$

$$\Rightarrow \hat{P}^2/\psi\rangle = /\psi_i\rangle\langle\psi_i||\psi\rangle = \hat{P}/\psi\rangle$$

$$\Rightarrow \hat{P}^2 = \hat{P}$$

70. Show that trace$Tr(\hat{A}\hat{B}) = Tr(\hat{B}\hat{A})$?

Solution

By definition

$$Tr(\hat{A}\hat{B}) = \sum_m \langle\psi_m|\hat{A}\hat{B}|\psi_m\rangle$$

$$Tr(\hat{A}\hat{B}) = \sum_m \left\langle \psi_m \middle| \hat{A}\left(\sum_n /\psi_n\rangle\langle\psi_n/\right)\hat{B} \middle| \psi_m \right\rangle$$

$$Tr(\hat{A}\hat{B}) = \sum_{m,n} \langle\psi_m|\hat{A}|\psi_n\rangle\langle\psi_n|\hat{B}|\psi_m\rangle = \sum_{m,n} \hat{A}_{mn}\hat{B}_{nm}$$

Similarly

$$Tr(\hat{B}\hat{A}) = \sum_n \langle\psi_n|\hat{B}\hat{A}|\psi_n\rangle$$

$$Tr(\hat{A}\hat{B}) = \sum_n \left\langle \psi_n \middle| \hat{B}\left(\sum_m /\psi_m\rangle\langle\psi_m/\right)\hat{A} \middle| \psi_n \right\rangle$$

$$Tr(\hat{B}\hat{A}) = \sum_{m,n} \langle\psi_n|\hat{B}|\psi_m\rangle\langle\psi_m|\hat{A}|\psi_n\rangle = \sum_{m,n} \hat{A}_{mn}\hat{B}_{nm}$$

$$\Rightarrow Tr(\hat{A}\hat{B}) = Tr(\hat{B}\hat{A})$$

71. Show that trace of an operator is independent of the basis?

Solution

By definition

$$Tr\hat{A} = \sum_m \langle\psi_m|\hat{A}|\psi_m\rangle$$

$$Tr\hat{A} = \sum_{m,n} \langle\psi_n|\psi_m\rangle\langle\psi_m|\hat{A}|\psi_m\rangle\langle\psi_m|\psi_n\rangle$$

$$Tr\hat{A} = \sum_m \langle\psi_m|\hat{A}|\psi_m\rangle\langle\psi_n|\psi_n\rangle = \sum_m \langle\psi_m|\hat{A}|\psi_m\rangle$$

So trace of an operator is independent of the basis.

72. Starting from the Eigen value equation $\hat{U}|\psi\rangle = a|\psi\rangle$. Here $\hat{U}$ is a unitary operator and a is Eigen value. Show that $a = e^{ic}$ here c is a real constant. Also prove the orthogonality of an Eigen vector of unitary operator?

Solution

As given

$$\hat{U}|\psi\rangle = a|\psi\rangle$$

Take adjoint

$$\langle\psi|\hat{U}^\dagger = a^*\langle\psi|$$

$$\langle\psi|\hat{U}^\dagger\hat{U}|\psi\rangle = a^*\langle\psi|a|\psi\rangle$$

$$\langle\psi|\psi\rangle = |a|^2\langle\psi|\psi\rangle \Rightarrow |a|^2 = 1$$

As if x is small then $e^x = 1$ so we can write $1 = e^{ic}$

$$\Rightarrow a = e^{ic}$$

Now let $|\Phi\rangle$ is another Eigen vector of $\hat{U}$ with corresponding eigen value b.Then

$$\hat{U}|\Phi\rangle = b|\Phi\rangle$$

Now $$\langle\psi|\Phi\rangle = \langle\psi|\hat{U}^\dagger\hat{U}|\Phi\rangle = a^*\langle\psi|b|\Phi\rangle$$

As $a = e^{ic}$ so $b = e^{iD}$ hence

$$\Rightarrow \langle\psi|\Phi\rangle = e^{-ic}e^{iD}\langle\psi|\Phi\rangle$$

$$\Rightarrow \langle\psi|\Phi\rangle\left(1 - e^{i(D-c)}\right) = 0$$

$$\Rightarrow either\ \langle\psi|\Phi\rangle = 0\ OR\ \left(1 - e^{i(D-c)}\right) = 0$$

But $\left(1-e^{i(D-c)}\right)\neq 0$ because $D\neq c$ So, $\langle\psi|\Phi\rangle=0$.This result shows both $|\Phi\rangle$ and $|\psi\rangle$ are orthogonal to each other.

73. Give the mathematical representation of a spherical wave travelling outward from a point and evaluate its probability current density.?

Solution

A spherical wave is represented by

$$\psi=\frac{A}{r}e^{ikr}$$

Now probability current density is given by

$$J=\frac{i\hbar}{2m}(\psi\nabla\psi^{*}-\psi^{*}\nabla\psi)$$

$$J=\frac{i\hbar}{2m}\left(\frac{A}{r}e^{ikr}\frac{\mathrm{d}}{\mathrm{dr}}\left(\frac{A}{r}e^{-ikr}\right)-\frac{A}{r}e^{-ikr}\frac{\mathrm{d}}{\mathrm{dr}}\left(\frac{A}{r}e^{ikr}\right)\right)$$

$$J=\frac{i\hbar}{2m}\frac{A}{r}\left(e^{ikr}\left\{-ike^{-ikr}\frac{A}{r}-\frac{A}{r^{2}}e^{-ikr}\right\}-e^{-ikr}\left\{ike^{ikr}\frac{A}{r}-\frac{A}{r^{2}}e^{ikr}\right\}\right)$$

$$J=\frac{i\hbar}{2m}\frac{A}{r}\left(-ik\frac{A}{r}-\frac{A}{r^{2}}-ik\frac{A}{r}+\frac{A}{r^{2}}\right)$$

$$J=\frac{i\hbar}{2m}\frac{A}{r}\left(-2ik\frac{A}{r}\right)=\frac{\hbar k}{m}\frac{|A|^{2}}{r^{2}}$$

74. The wave function of a particle of mass m moving in a potential $V(x)$ is

$\psi(x,t)=Ae^{\left(-ikt-\frac{kmx^{2}}{\hbar}\right)}$ Where A and k are constants. Find the explicit form of the potential$V(x)$?

Solution

As Schrodinger's equation is

$$i\hbar\frac{\partial\psi}{\partial t}=\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+V\psi$$

$$i\hbar\frac{\partial}{\partial t}Ae^{\left(-ikt-\frac{kmx^2}{\hbar}\right)}=\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}Ae^{\left(-ikt-\frac{kmx^2}{\hbar}\right)}+V\psi$$

$$i\hbar(-ik)Ae^{\left(-ikt-\frac{kmx^2}{\hbar}\right)}=\frac{-\hbar^2}{2m}\left(-\frac{2km}{\hbar}\right)\frac{\partial}{\partial x}Axe^{\left(-ikt-\frac{kmx^2}{\hbar}\right)}+V\psi$$

$$\hbar kAe^{\left(-ikt-\frac{kmx^2}{\hbar}\right)}=\frac{-\hbar^2}{2m}\left(-\frac{2km}{\hbar}\right)\frac{\partial}{\partial x}Axe^{\left(-ikt-\frac{kmx^2}{\hbar}\right)}+V\psi$$

CHAPTER 5

ANGULAR MOMENTUM AND SPIN

Just like position, energy and momentum etc. in quantum mechanics called as operator. Similarly in quantum mechanics angular momentum is also used an operator called angular momentum operator. There are three types of angular momentum operators

1. Orbital angular momentum$\hat{L}$
2. Spin angular momentum $\hat{S}$
3. Total angular momentum$\hat{J}$

Relation

As classically

$$\boldsymbol{L}=\boldsymbol{r}\boldsymbol{x}\boldsymbol{P}$$

$$\boldsymbol{L}=\begin{vmatrix}\hat{\imath} & \hat{\jmath} & \hat{k}\\ \boldsymbol{x} & \boldsymbol{y} & \boldsymbol{z}\\ \boldsymbol{P_x} & \boldsymbol{P_y} & \boldsymbol{P_z}\end{vmatrix}$$

I**n** quantum mechanics

$$\hat{L}=\hat{r}\boldsymbol{x}\hat{P}$$

$$\hat{L} = \begin{vmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{P}_x & \hat{P}_y & \hat{P}_z \end{vmatrix}$$

$$\hat{L}_x\hat{\imath} + \hat{L}_y\hat{\jmath} + \hat{L}_z\hat{k} = \hat{\imath}\left(\hat{y}\hat{P}_z - \hat{z}\hat{P}_y\right) - \hat{\jmath}\left(\hat{x}\hat{P}_z - \hat{z}\hat{P}_x\right) + \hat{k}\left(\hat{x}\hat{P}_y - \hat{y}\hat{P}_x\right)$$

Compering the coefficients of$\hat{\imath}, \hat{\jmath}\ and\ \hat{k}$

$$\hat{L}_x = \left(\hat{y}\hat{P}_z - \hat{z}\hat{P}_y\right) \text{ ----------}\mathbf{1}$$

$$\hat{L}_y = \left(\hat{z}\hat{P}_x - \hat{x}\hat{P}_z\right) \text{ ----------}\mathbf{2}$$

$$\hat{L}_z = \left(\hat{x}\hat{P}_y - \hat{y}\hat{P}_x\right) \text{ ----------}\mathbf{3}$$

But

$$\hat{P}_x = -i\hbar\frac{\partial}{\partial x}\ , \qquad \hat{P}_y = -i\hbar\frac{\partial}{\partial y}\ , \qquad \hat{P}_z = -i\hbar\frac{\partial}{\partial}$$

So equations 1, 2 and 3 will be

$$\hat{L}_x = i\hbar\left(\hat{z}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial z}\right) \text{ ----------}\mathbf{4}$$

$$\hat{L}_y = i\hbar\left(\hat{x}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial x}\right) \text{ ----------}\mathbf{5}$$

$$\hat{L}_z = i\hbar\left(\hat{y}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial y}\right) \text{ ----------}\mathbf{6}$$

Similarly for Spin angular momentum

$$\hat{S}_x = i\hbar\left(\hat{z}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial z}\right) \text{ ----------}\mathbf{7}$$

$$\hat{S}_y = i\hbar\left(\hat{x}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial x}\right) \text{ ----------}\mathbf{8}$$

$$\hat{S}_z = i\hbar\left(\hat{y}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial y}\right) \text{ ----------}\mathbf{9}$$

For total angular momentum

$$\hat{J}_x = i\hbar\left(\hat{z}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial z}\right) \text{ ----------}\mathbf{10}$$

$$\hat{J}_y = i\hbar\left(\hat{x}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial x}\right) \text{ ----------11}$$

$$\hat{J}_z = i\hbar\left(\hat{y}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial y}\right) \text{ ----------12}$$

Angular momentum commutation relations

1. $\left[\widehat{L}_x, \widehat{L}_y\right] = i\hbar\widehat{L}_z$
2. $\left[\widehat{L}_y, \widehat{L}_z\right] = i\hbar\widehat{L}_x$
3. $\left[\widehat{L}_z, \widehat{L}_x\right] = i\hbar\widehat{L}_y$
4. $\left[\widehat{L}^2, \widehat{L}_x\right] = 0$
5. $\left[\widehat{L}^2, \widehat{L}_y\right] = 0$
6. $\left[\widehat{L}^2, \widehat{L}_z\right] = 0$
7. $\left[\widehat{L}_x, \hat{x}\right] = 0$
8. $\left[\widehat{L}_y, \hat{y}\right] = 0$
9. $\left[\widehat{L}_z, \hat{z}\right] = 0$

Similarly replace $\widehat{L}$ with $\hat{S}$ and $\hat{J}$ for spin and total angular momentum respectively.

Proofs

1. $\left[\widehat{L}_x, \widehat{L}_y\right] = i\hbar\widehat{L}_z$

As

$$\hat{L}_x = \left(\hat{y}\hat{P}_{\boldsymbol{z}} - \hat{z}\hat{P}_{\boldsymbol{y}}\right) \text{ ----------1}$$

$$\hat{L}_y = \left(\hat{z}\hat{P}_{\boldsymbol{x}} - \hat{x}\hat{P}_{\boldsymbol{z}}\right) \text{ ----------2}$$

$$\hat{L}_z = \left(\hat{x}\hat{P}_{\boldsymbol{y}} - \hat{y}\hat{P}_{\boldsymbol{x}}\right) \text{ ----------3}$$

So $$\left[\widehat{L}_x, \widehat{L}_y\right] = \left[\left(\hat{y}\hat{P}_{\boldsymbol{z}} - \hat{z}\hat{P}_{\boldsymbol{y}}\right), \left(\hat{z}\hat{P}_{\boldsymbol{x}} - \hat{x}\hat{P}_{\boldsymbol{z}}\right)\right]$$

By using the property of commutator brackets

$$\left[\hat{L}_x, \hat{L}_y\right] = \left[\hat{y}\hat{P}_z, \hat{z}\hat{P}_x - \hat{x}\hat{P}_z\right] - \left[\hat{z}\hat{P}_y, \hat{z}\hat{P}_x - \hat{x}\hat{P}_z\right]$$

$$\left[\hat{L}_x, \hat{L}_y\right] = \left[\hat{y}\hat{P}_z, \hat{z}\hat{P}_x\right] - \left[\hat{y}\hat{P}_z, \hat{x}\hat{P}_z\right] - \left[\hat{z}\hat{P}_y, \hat{z}\hat{P}_x\right] + \left[\hat{z}\hat{P}_y, \hat{x}\hat{P}_z\right]$$

As $$\left[\hat{y}\hat{P}_z, \hat{x}\hat{P}_z\right] = \left[\hat{z}\hat{P}_y, \hat{z}\hat{P}_x\right] = 0$$

So

$$\left[\hat{L}_x, \hat{L}_y\right] = \left[\hat{y}\hat{P}_z, \hat{z}\hat{P}_x\right] + \left[\hat{z}\hat{P}_y, \hat{x}\hat{P}_z\right]$$

$$\left[\hat{L}_x, \hat{L}_y\right] = \hat{y}\hat{P}_x\left[\hat{P}_z, \hat{z}\right] + \hat{x}\hat{P}_y\left[\hat{z}, \hat{P}_z\right]$$

As $$\left[\hat{z}, \hat{P}_z\right] = i\hbar$$

So

$$\left[\hat{L}_x, \hat{L}_y\right] = \hat{y}\hat{P}_x(-\boldsymbol{i}\hbar) + \hat{x}\hat{P}_y(i\hbar)$$

$$\left[\hat{L}_x, \hat{L}_y\right] = \boldsymbol{i}\hbar(\hat{x}\hat{P}_y - \hat{y}\hat{P}_x)$$

$$\left[\hat{L}_x, \hat{L}_y\right] = \boldsymbol{i}\hbar\hat{L}_z$$

Similarly

$$\left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x$$
$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$$

Now we have to prove $\left[\hat{L}^2, \hat{L}_x\right] = 0$

Proof

$$\left[\hat{L}^2, \hat{L}_x\right] = \left[\hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2, \hat{L}_x\right]$$

$$\left[\hat{L}^2, \hat{L}_x\right] = \left[\hat{L}_x{}^2, \hat{L}_x\right] + \left[\hat{L}_y{}^2, \hat{L}_x\right] + \left[\hat{L}_z{}^2, \hat{L}_x\right]$$

As $\left[\hat{L}_x{}^2, \hat{L}_x\right] = 0$

So

$$\left[\hat{L}^2, \hat{L}_x\right] = \left[\hat{L}_y{}^2, \hat{L}_x\right] + \left[\hat{L}_z{}^2, \hat{L}_x\right]$$

Using property $\left[\hat{A}^2, \hat{B}\right] = \hat{A}\left[\hat{A}, \hat{B}\right] + \left[\hat{A}, \hat{B}\right]\hat{A}$

$$\left[\hat{L}^2, \hat{L}_x\right] = \hat{L}_y\left[\hat{L}_y, \hat{L}_x\right] + \left[\hat{L}_y, \hat{L}_x\right]\hat{L}_y + \hat{L}_z\left[\hat{L}_z, \hat{L}_x\right] + \left[\hat{L}_z, \hat{L}_x\right]\hat{L}_z$$

$$\left[\hat{L}^2, \hat{L}_x\right] = \hat{L}_y\left(-i\hbar\hat{L}_z\right) + \left(-i\hbar\hat{L}_z\right)\hat{L}_y + \hat{L}_z\left(i\hbar\hat{L}_y\right) + \left(i\hbar\hat{L}_y\right)\hat{L}_z$$

$$\left[\hat{L}^2, \hat{L}_x\right] = -i\hbar\hat{L}_y\hat{L}_z - i\hbar\hat{L}_z\hat{L}_y + i\hbar\hat{L}_z\hat{L}_y + i\hbar\hat{L}_y\hat{L}_z$$

$$\left[\hat{L}^2, \hat{L}_x\right] = 0$$

Similarly $\left[\hat{L}^2, \hat{L}_y\right] = \left[\hat{L}^2, \hat{L}_z\right] = 0$

Now we have to prove that $\left[\hat{L}_x, \hat{x}\right] = 0$

Proof

As $$\left[\hat{L}_x, \hat{x}\right] = \hat{L}_x\hat{x} - \hat{x}\hat{L}_x$$

Multiply both sides by $/\psi_x >$

$$\left[\hat{L}_x, \hat{x}\right]/\psi_x >= \hat{L}_x\hat{x}/\psi_x > -\hat{x}\hat{L}_x/\psi_x >$$

$$\left[\hat{L}_x, \hat{x}\right]/\psi_x >= i\hbar\left(\hat{z}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial z}\right)\hat{x}/\psi_x > -\hat{x}i\hbar\left(\hat{z}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial z}\right)/\psi_x >$$

Now derivative of $\hat{x}/\psi_x >$ with respect to y and z is zero.

So $$\left[\hat{L}_x, \hat{x}\right]/\psi_x >= 0$$

$$\left[\hat{L}_x, \hat{x}\right] = 0$$

Similarly $$\left[\hat{L}_y, \hat{y}\right] = \left[\hat{L}_z, \hat{z}\right] = 0$$

Eigen values of angular momentum

1. Orbital angular momentum Eigen value

i. $\widehat{L}_x = m_l\hbar$ here $m_l = 0, \mp1, \mp2, --$

ii. $\widehat{L}_y = m_l\hbar$ $m_l = megnetic\ quantum\ number$

iii. $\widehat{L}_z = m_l\hbar$

iv. $\widehat{L^2} = l(l+1)\hbar^2$ here $l = 0,1,2, --n-1$

v. $\hat{L}^2 = \sqrt{l(l+1)}\hbar$ $l = Azimothal\ quantum\ number$

2. Spin angular momentumEigen value

i. $\widehat{S}_x = m_s\hbar$ here $m_s = 0, \mp\frac{1}{2}, \mp1, --$

ii. $\widehat{S}_y = m_s\hbar$ $m_s = megnetic\ spin\ quantum\ number$

iii. $\widehat{S}_{z=} m_s\hbar$

iv. $\hat{S} = s(s+1)\hbar^2$ here $s = 0, \frac{1}{2}, 1--$

v. $\hat{S}^2 = \sqrt{s(s+1)}\hbar$ $s = spin\ quantum\ number$

3. Total angular momentum Eigen value

i. $\widehat{J}_x = m_j\hbar$ here $m_j = 0, \mp\frac{1}{2}, \mp1, --$

ii. $\widehat{J}_y = m_j\hbar$ $m_j = Total\ megnetic\ spin\ projection\ quantum\ number$

iii. $\widehat{J}_z = m_j\hbar$

iv. $\hat{J} = j(j+1)\hbar^2$ here $j = 0, \frac{1}{2}, 1--$

v. $\hat{J}^2 = \sqrt{j(j+1)}\hbar$ $j = Total\ megnetic\ spin\ quantum\ number$

Angular momentum in spherical polar coordinates

We know that relation between Cartesian coordinates (x,y,z) and spherical polar coordinates are

$$x = r\sin\theta\cos\emptyset$$

$$y = r\sin\theta\sin\emptyset$$

$$z = r\cos\theta$$

And in spherical polar coordinates

$$\nabla = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\emptyset}\frac{1}{r\sin\theta}\frac{\partial}{\partial \emptyset}$$

I**n** quantum mechanics

$$\hat{L} = \vec{r} \times \hat{P}$$

$$\hat{L} = \vec{r} \times -i\hbar\nabla$$

$$\hat{L} = -\boldsymbol{i}\hbar \begin{vmatrix} \hat{r} & \hat{\theta} & \hat{\emptyset} \\ r & 0 & 0 \\ \frac{\partial}{\partial r} & \frac{1}{r}\frac{\partial}{\partial \theta} & \frac{1}{r\sin\theta}\frac{\partial}{\partial \emptyset} \end{vmatrix}$$

$$\hat{L} = -\boldsymbol{i}\hbar\left[\hat{r}(0-0) + \hat{\theta}\left(0 - \frac{r}{r\sin\theta}\frac{\partial}{\partial \emptyset}\right) + \hat{\emptyset}(\frac{r}{r}\frac{\partial}{\partial \theta} - 0)\right]$$

$$\hat{L} = -\boldsymbol{i}\hbar\left(-\frac{\hat{\theta}}{\sin\theta}\frac{\partial}{\partial \emptyset} + \hat{\emptyset}\frac{\partial}{\partial \theta}\right)$$

This is angular momentum operator in spherical polar coordinate.

Now we find L^2 in spherical polar coordinates.

As $$L^2 = L.L = (r\hat{r} \times -i\hbar\nabla).(r\hat{r} \times -i\hbar\nabla)$$

$$L^2 = -\hbar^2(r\hat{r} \times \nabla).(r\hat{r} \times -\nabla)$$

$$L^2 = -\hbar^2 r^2(\nabla^2 - \frac{1}{\mathrm{r}^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right))$$

$$L^2 = -\hbar^2 r^2(\nabla^2 - \frac{1}{\mathrm{r}^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right))$$

Now ∇^2 in spherical polar coordinates is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

So

$$L^2 = -\hbar^2 r^2(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\eth}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2} - \frac{1}{\mathrm{r}^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right))$$

$$L^2 = -\hbar^2 \left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right\}$$

Now we find the values of $\boldsymbol{L_x}$, $\boldsymbol{L_y}$, $\boldsymbol{L_z}$ in spherical polar coordinates

We know that in spherical polar coordinates values of unit vectors

$$\hat{\imath} = \sin\theta\cos\emptyset\,\hat{r} + \cos\theta\cos\emptyset\,\hat{\theta} - \sin\emptyset\,\hat{\emptyset}$$

$$\hat{\jmath} = \sin\theta\sin\emptyset\,\hat{r} + \cos\theta\sin\emptyset\,\hat{\theta} + \cos\emptyset\,\hat{\emptyset}$$

$$\hat{k} = \cos\theta\,\hat{r} - \sin\theta\,\hat{\theta}$$

Now in spherical polar coordinates

$$\hat{L} = -\boldsymbol{i}\hbar \left(-\frac{\hat{\theta}}{\sin\theta} \frac{\partial}{\partial\emptyset} + \hat{\emptyset} \frac{\partial}{\partial\theta} \right)$$

Now

$$\vec{L} = \boldsymbol{L_x}\hat{\imath} + \boldsymbol{L_y}\hat{\jmath} + \boldsymbol{L_z}\hat{k}$$

$$\overrightarrow{\hat{\imath}.L} = \hat{\imath}.(\boldsymbol{L_x}\hat{\imath} + \boldsymbol{L_y}\hat{\jmath} + \boldsymbol{L_z}\hat{k})$$

$$\hat{\imath}.\vec{L} = \boldsymbol{L_x} = \{\sin\theta\cos\emptyset\,\hat{r} + \cos\theta\cos\emptyset\,\hat{\theta} - \sin\emptyset\,\hat{\emptyset}\}.\left\{ -\boldsymbol{i}\hbar \left(-\frac{\hat{\theta}}{\sin\theta} \frac{\partial}{\partial\emptyset} + \hat{\emptyset} \frac{\partial}{\partial\theta} \right) \right\}$$

$$\boldsymbol{L_x} = -\boldsymbol{i}\hbar \left(-\sin\emptyset \frac{\partial}{\partial\theta} - \frac{\cos\theta}{\sin\theta} \cos\emptyset \frac{\partial}{\partial\emptyset} \right)$$

$$\boldsymbol{L_x} = \boldsymbol{i}\hbar \left(\sin\emptyset \frac{\partial}{\partial\theta} - \cot\theta\cos\emptyset \frac{\partial}{\partial\emptyset} \right)$$

Similarly

$$\boldsymbol{L_y} = \hat{\jmath}.\vec{L} = \{\sin\theta\sin\emptyset\,\hat{r} + \cos\theta\sin\emptyset\,\hat{\theta} + \cos\emptyset\,\hat{\emptyset}\}.\left\{ -\boldsymbol{i}\hbar \left(-\frac{\hat{\theta}}{\sin\theta} \frac{\partial}{\partial\emptyset} + \hat{\emptyset} \frac{\partial}{\partial\theta} \right) \right\}$$

$$\boldsymbol{L_y} = \boldsymbol{i}\hbar \left(-\cos\emptyset \frac{\partial}{\partial\theta} - \cot\theta\sin\emptyset \frac{\partial}{\partial\emptyset} \right)$$

And

$$\boldsymbol{L_z} = \hat{k}.\vec{L} = \{\cos\theta\,\hat{r} - \sin\theta\,\hat{\theta}\}.\left\{-\boldsymbol{i}\hbar\left(-\frac{\hat{\theta}}{\sin\theta}\frac{\partial}{\partial\emptyset} + \hat{\emptyset}\frac{\partial}{\partial\theta}\right)\right\}$$

$$\boldsymbol{L_z} = -\boldsymbol{i}\hbar\frac{\partial}{\partial\emptyset}$$

Eigen Value of $\boldsymbol{L_z}$

Let λ is the eigen value of L_z corresponding to the wave function ψ. So we can write

$$\boldsymbol{L_z}\psi = \lambda\,\psi$$

But

$$\boldsymbol{L_z} = -\boldsymbol{i}\hbar\frac{\partial}{\partial\emptyset}$$

So

$$-\boldsymbol{i}\hbar\frac{\partial\psi}{\partial\emptyset} = \lambda\,\psi$$

$$\frac{d\psi}{\psi} = \frac{\lambda d\emptyset}{-\boldsymbol{i}\hbar}$$

Integrate both sides

$$\int_A^{\psi}\frac{d\psi}{\psi} = \frac{\boldsymbol{i}\lambda}{\hbar}\int_0^{\phi} d\emptyset$$

$$|\boldsymbol{ln}(\psi)|_A^{\psi} = \frac{\boldsymbol{i}\lambda}{\hbar}|\emptyset|_0^{\emptyset}$$

$$\boldsymbol{ln}(\psi) - \boldsymbol{ln}(A) = \frac{\boldsymbol{i}\lambda\emptyset}{\hbar}$$

$$\boldsymbol{ln}\frac{\psi}{A} = \frac{\boldsymbol{i}\lambda\emptyset}{\hbar}$$

$$\psi = Ae^{\frac{\boldsymbol{i}\lambda\emptyset}{\hbar}}$$

This is the Eigen function of $\boldsymbol{L_z}$.

As by definition ψ must be single valued, continuous, finite and non zero and in one cycle $\emptyset$ changes from 0 to 2π. Therefore we can write for single value

$$\psi(\emptyset) = \psi(\emptyset + 2\pi)$$

$$Ae^{\frac{i\lambda\emptyset}{\hbar}} = Ae^{\frac{i\lambda(\emptyset+2\pi)}{\hbar}}$$

$$e^{\frac{i\lambda 2\pi}{\hbar}} = 1$$

As $e^{i2m\pi} = \cos(2m\pi) + i\sin(2m\pi) = 1$ so we can write

$$e^{\frac{i\lambda 2\pi}{\hbar}} = e^{i2m}$$

$$\frac{i\lambda 2\pi}{\hbar} = i2m\pi$$

$$\Rightarrow \lambda = m\hbar$$

This is the eigen value of $\boldsymbol{L_z}$**.** So we can write

$$\boldsymbol{L_z}\psi = m\hbar\,\psi$$

Ladder operator or Shift operator

In quantum mechanics ladder operator is an operator which increases or decreases the Eigen value by one. When Eigen value increases by 1 then ladder operator is called raising operator or step up operator and when Eigen value decreases by 1 the ladder operator is called lowering operator or step down operator. Ladder operator is used to describe the motion of simple harmonic oscillator where energy is increases and decreased during oscillations. Similarly to describe the angular momentum states and many particles systems where we have to increase or decrease the number of particles.

Ladder operator in angular momentum

In angular momentum, ladder operators are written as

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \quad \text{And} \quad \hat{L}_- = \hat{L}_x - i\hat{L}_y$$

Here $\hat{L}_+$ is called raising operator and $\hat{L}_-$ is called lowering operator.

Commutation relations

1. $\left[\hat{L}^2, \hat{L}_+\right] = 0$
2. $\left[\hat{L}^2, \hat{L}_-\right] = 0$
3. $\left[\hat{L}_z, \hat{L}_+\right] = -\hbar\hat{L}_+$
4. $\left[\hat{L}_z, \hat{L}_-\right] = -\hbar\hat{L}_-$
5. $\left[\hat{L}_+, \hat{L}_-\right] = -2\hbar\hat{L}_z$
6. $\left[\hat{L}_-, \hat{L}_+\right] = 2\hbar\hat{L}_z$

Proof

1. $\left[\hat{L}^2, \hat{L}_+\right] = 0$
2. $\left[\hat{L}^2, \hat{L}_-\right] = 0$

Now $$\left[\hat{L}^2, \hat{L}_+\right] = \left[\hat{L}^2, \hat{L}_x + i\hat{L}_y\right]$$

$$\left[\hat{L}^2, \hat{L}_+\right] = \left[\hat{L}^2, \hat{L}_x\right] + i\left[\hat{L}^2, \hat{L}_y\right]$$

But $\left[\hat{L}^2, \hat{L}_x\right] = \left[\hat{L}^2, \hat{L}_y\right] = 0$

So $$\left[\hat{L}^2, \hat{L}_+\right] = 0$$

Similarly $$\left[\hat{L}^2, \hat{L}_-\right] = 0$$

Proof

3. $\left[\hat{L}_z, \hat{L}_+\right] = -\hbar\hat{L}_+$
4. $\left[\hat{L}_z, \hat{L}_-\right] = -\hbar\hat{L}_-$

Now

$$\left[\hat{L}_z, \hat{L}_+\right] = \hat{L}_z\hat{L}_+ - \hat{L}_+\hat{L}_z$$

$$\left[\hat{L}_z, \hat{L}_+\right] = \hat{L}_z\left(\hat{L}_x + i\hat{L}_y\right) - \left(\hat{L}_x + i\hat{L}_y\right)\hat{L}_z$$

$$\left[\hat{L}_z, \hat{L}_+\right] = \hat{L}_z\hat{L}_x + i\hat{L}_z\hat{L}_y - \hat{L}_x\hat{L}_z - i\hat{L}_y\hat{L}_z$$

$$\left[\hat{L}_z, \hat{L}_+\right] = \left[\hat{L}_z, \hat{L}_x\right] + i\left[\hat{L}_z, \hat{L}_y\right]$$

But $\left[\hat{L}_z, \hat{L}_x\right] = -i\hbar\hat{L}_y$ and $\left[\hat{L}_z, \hat{L}_y\right] = i\hbar\hat{L}_x$

So

$$\left[\hat{L}_z, \hat{L}_+\right] = -i\hbar\hat{L}_y + i\left(i\hbar\hat{L}_x\right)$$
$$\left[\hat{L}_z, \hat{L}_+\right] = -i\hbar\hat{L}_y - \hbar\hat{L}_x$$
$$\left[\hat{L}_z, \hat{L}_+\right] = -\hbar\left(\hat{L}_x + i\hat{L}_y\right)$$
$$\left[\hat{L}_z, \hat{L}_+\right] = -\hbar\hat{L}_+$$

Similarly

$$\left[\hat{L}_z, \hat{L}_-\right] = -\hbar\hat{L}_-$$

Proofs

5. $\left[\hat{L}_+, \hat{L}_-\right] = -2\hbar\hat{L}_z$
6. $\left[\hat{L}_-, \hat{L}_+\right] = 2\hbar\hat{L}_z$

Now

$$\left[\hat{L}_+, \hat{L}_-\right] = \hat{L}_+\hat{L}_- - \hat{L}_-\hat{L}_+$$
$$\left[\hat{L}_+, \hat{L}_-\right] = \left(\hat{L}_x + i\hat{L}_y\right)\left(\hat{L}_x - i\hat{L}_y\right) - \left(\hat{L}_x - i\hat{L}_y\right)\left(\hat{L}_x + i\hat{L}_y\right)$$
$$\left[\hat{L}_+, \hat{L}_-\right] = \left(\hat{L}_x + i\hat{L}_y\right)\left(\hat{L}_x - i\hat{L}_y\right) - \left(\hat{L}_x - i\hat{L}_y\right)\left(\hat{L}_x + i\hat{L}_y\right)$$
$$\left[\hat{L}_+, \hat{L}_-\right] = \hat{L}_x^{\,2} - i\hat{L}_x\hat{L}_y + i\hat{L}_y\hat{L}_x + \hat{L}_y^{\,2} - \hat{L}_x^{\,2} - i\hat{L}_x\hat{L}_y + i\hat{L}_y\hat{L}_x - \hat{L}_y^{\,2}$$
$$\left[\hat{L}_+, \hat{L}_-\right] = -i\hat{L}_x\hat{L}_y + i\hat{L}_y\hat{L}_x - i\hat{L}_x\hat{L}_y + i\hat{L}_y\hat{L}_x$$
$$\left[\hat{L}_+, \hat{L}_-\right] = -i\left(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x\right) - i\left(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x\right)$$
$$\left[\hat{L}_+, \hat{L}_-\right] = -2i\left(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x\right)$$
$$\left[\hat{L}_+, \hat{L}_-\right] = -2i\left[\hat{L}_x, \hat{L}_y\right]$$
$$\left[\hat{L}_+, \hat{L}_-\right] = -2i\left(-i\hbar\hat{L}_z\right)$$
$$\left[\hat{L}_+, \hat{L}_-\right] = -2\hbar\hat{L}_z$$

Similarly

$$\left[\hat{L}_-, \hat{L}_+\right] = 2\hbar\hat{L}_z$$

Eigen value of angular momentum $\hat{L}$

Prove that $\hat{L} = \sqrt{l(l+1)}\hbar$

Proof

As$\hat{L}_+\hat{L}_- = \left(\hat{L}_x + i\hat{L}_y\right)\left(\hat{L}_x - i\hat{L}_y\right)$

$$\hat{L}_+\hat{L}_- = \hat{L}_x{}^2 - i\hat{L}_x\hat{L}_y + i\hat{L}_y\hat{L}_x + \hat{L}_y{}^2$$

$$\hat{L}_+\hat{L}_- = \hat{L}_x{}^2 + \hat{L}_y{}^2 - i(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x)$$

$$\hat{L}_+\hat{L}_- = \hat{L}_x{}^2 + \hat{L}_y{}^2 - i\left[\hat{L}_x, \hat{L}_y\right)]$$

$$\hat{L}_+\hat{L}_- = \hat{L}_x{}^2 + \hat{L}_y{}^2 - i(-i\hbar\hat{L}_z)$$

$\hat{L}_+\hat{L}_- = \hat{L}_x{}^2 + \hat{L}_y{}^2 - \hbar\hat{L}_z$---------- (1)

We Know That

$$\hat{L}^2 = \hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2$$

$$\hat{L}_x{}^2 + \hat{L}_y{}^2 = \hat{L}^2 - \hat{L}_z{}^2$$

So equation 1 will become

$$\hat{L}_+\hat{L}_- = \hat{L}^2 - \hat{L}_z{}^2 - \hbar\hat{L}_z$$

$$\hat{L}^2 = \hat{L}_z{}^2 + \hbar\hat{L}_z + \hat{L}_+\hat{L}_-$$

Let $/\psi>$ is the wave function of the operator $\hat{L}^2$ then we can write

$$\hat{L}^2/\psi> = \hat{L}_z{}^2/\psi> + \hbar\hat{L}_z/\psi> + \hat{L}_+\hat{L}_-/\psi>$$

As $\hat{L}_z/\psi> = l\hbar$, $\hat{L}_z{}^2/\psi> = l^2\hbar^2$ and $\hat{L}_+\hat{L}_-/\psi> = 0$

So

$$\hat{L}^2/\psi >= l^2\hbar^2/\psi > +l\hbar^2/\psi > +0$$

$$\hat{L}^2/\psi >= l(l+1)\hbar^2/\psi >$$

$$\Rightarrow \hat{\boldsymbol{L}}/\psi >= \sqrt{l(l+1)}\hbar/\psi >$$

So This is Eigen value of $\hat{\boldsymbol{L}}$ **is** $\sqrt{l(l+1)}\hbar$

Eigen function of $\hat{\boldsymbol{L}}^2$ and $\hat{\boldsymbol{L}}_{\boldsymbol{z}}$ and spherical harmonics

Let ψ_{lm} is the simultaneous eign function of $\hat{L}^2$ and $\hat{L}_z$.So Eigen value equations will be

$$\hat{L}^2\psi_{lm} = l(l+1)\hbar^2\psi_{lm}\text{------(1)}$$

$$\hat{L}_z\psi_{lm} = m\hbar\psi_{lm}\text{ ------- (2)}$$

In spherical polar coordinates equation (2) will be

$$-\boldsymbol{i}\hbar\frac{\partial\psi_{lm}}{\partial\emptyset} = m\hbar\,\psi_{lm}\text{------- (3)}$$

By variable separable method we can have

$$\psi_{lm} = \boldsymbol{\theta}_{(\theta)}\emptyset_{(\emptyset)} = \boldsymbol{\theta}e^{im\emptyset}$$

Sp equation (1) can be written as

$$\hat{L}^2\boldsymbol{\theta}e^{im\emptyset} = l(l+1)\hbar^2\boldsymbol{\theta}e^{im\emptyset}$$

$$\hat{L}^2\boldsymbol{\theta}e^{im\emptyset} = l(l+1)\hbar^2\boldsymbol{\theta}e^{im\emptyset}$$

As in spherical polar coordinates

$$L^2 = -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}$$

So

$$-\hbar^2\left\{\frac{e^{im\emptyset}}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right)+\frac{\boldsymbol{\theta}}{\sin^2\theta}\frac{\partial^2 e^{im\emptyset}}{\partial\phi^2}\right\} = l(l+1)\hbar^2\boldsymbol{\theta}e^{im\emptyset}$$

$$-\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right)-\frac{m^2\boldsymbol{\theta}}{\sin^2\theta}\right\}e^{im\emptyset} = l(l+1)\hbar^2\boldsymbol{\theta}e^{im\emptyset}$$

$$-\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right)-\frac{m^2\boldsymbol{\theta}}{\sin^2\theta}\right\} = l(l+1)\hbar^2\boldsymbol{\theta}$$

$$\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right)-\frac{m^2\boldsymbol{\theta}}{\sin^2\theta}\right\}+l(l+1)\hbar^2\boldsymbol{\theta} = \mathbf{0}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right)+\left\{l(l+1)\hbar^2-\frac{m^2}{\sin^2\theta}\right\}\boldsymbol{\theta}=\mathbf{0}$$

This is special type of differential equation. We solve it by substitution method.

Let $x=\cos\theta$

$$\frac{\partial}{\partial\theta}=\frac{\partial}{\partial x}\frac{\partial x}{\partial\theta}=-\sin\theta\frac{\partial}{\partial x}$$

So above equation will become

$$\frac{1}{\sin\theta}\left(-\sin\theta\frac{\partial}{\partial x}\right)\left(\sin\theta\left(-\sin\theta\frac{\partial}{\partial x}\right)\boldsymbol{\theta}\right)+\left\{l(l+1)-\frac{\mathrm{m}^2}{1-\cos^2\theta}\right\}\boldsymbol{\theta}=0$$

$$\frac{\eth}{\eth x}\left(\sin^2\theta\frac{\partial\boldsymbol{\theta}}{\partial x}\right)+\left\{l(l+1)-\frac{\mathrm{m}^2}{1-\cos^2\theta}\right\}\boldsymbol{\theta}=0$$

$$\frac{\eth}{\eth x}\left((1-\cos^2\theta)\frac{\partial\boldsymbol{\theta}}{\partial x}\right)+\left\{l(l+1)-\frac{\mathrm{m}^2}{1-\cos^2\theta}\right\}\boldsymbol{\theta}=0$$

$$\frac{\eth}{\eth x}\left((1-x^2)\frac{\partial\boldsymbol{\theta}}{\partial x}\right)+\left\{l(l+1)-\frac{\mathrm{m}^2}{1-x^2}\right\}\boldsymbol{\theta}=0$$

$$(1-x^2)\frac{\partial^2\boldsymbol{\theta}}{\partial x^2}-2x\frac{\partial\boldsymbol{\theta}}{\partial x}+\left\{l(l+1)-\frac{\mathrm{m}^2}{1-x^2}\right\}\boldsymbol{\theta}=0$$

This is associated Legendre's polynomial equation whose solution is

$$\boldsymbol{\theta}=C_{lm}\,P_l^m(x)=\frac{(1-x^2)^{\frac{m}{2}}}{2^l l!}\frac{\eth^{m+l}}{\eth x^{m+l}}(x^2-1)^l$$

So Simultaneous Eigen functions of $\hat{L}^2$ and $\hat{L}_z$ will be

$$\psi_{lm}=\boldsymbol{\theta}_{(\theta)}\emptyset_{(\emptyset)}=\boldsymbol{\theta}e^{im\emptyset}=C_{lm}\,P_l^m e^{im\emptyset}$$

$$C_{lm}\,P_l^m(x)e^{im\emptyset}=\;Y_l^m(\theta,\emptyset)$$

$Y_l^m(\theta,\emptyset)$ is called spherical harmonics. Now we find the value of C_{lm} by normalization.

$$\int\;Y_l^{m*}(\theta,\emptyset)\,Y_l^m(\theta,\emptyset)d\theta d\emptyset=1$$

$$\int_0^{2\pi}\int_0^{\pi}C_{lm}{}^*P_l^{m^*}e^{-im\emptyset}\,C_{lm}\,P_l^m e^{im\emptyset}d\theta d\emptyset=1$$

$$2\pi|C_{lm}|^2 \int_0^{\pi} P_l^{m*} P_l^m d\theta = 1$$

As

$$\int_0^{\pi} P_l^{m*} P_l^m d\theta = \frac{2(l+m)!}{(2l+1)(l-m)!}$$

Therefore

$$2\pi|C_{lm}|^2 \frac{2(l+m)!}{(2l+1)(l-m)!} = 1$$

$$|C_{lm}|^2 = \frac{(2l+1)(l-m)!}{4\pi(l+m)!}$$

$$C_{lm} = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}$$

There fore

$$Y_l^m(\theta, \emptyset) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(cos\theta) e^{im\emptyset}$$

$$Y_l^m(\theta, \emptyset) = (-\mathbf{1})^{\boldsymbol{m}} \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(cos\theta) e^{im\emptyset}$$

The extra factor $(-1)^m$ is included here, It is not necessary but in certain quantum mechanical problems it is convenient, It is called Condon- Shortly phase factor**.**

Eigen values of $\boldsymbol{L_+}$ and $\boldsymbol{L_-}$

OR show that

$$\boldsymbol{L_+}\psi_{lm} = \sqrt{l(l+1) - m(m+1)}\ \hbar\ \psi_{(l,m+1)}$$

$$\boldsymbol{L_-}\psi_{lm} = \sqrt{l(l+1) - m(m+1)}\ \hbar\ \psi_{(l,m-1)}$$

We know that

$$\hat{L}^2\psi_{lm} = l(l+1)\hbar^2\psi_{lm} \text{------ (1)}$$

$$\hat{L}_z\psi_{lm} = m\hbar\psi_{lm} \text{------- (2)}$$

We operate $\boldsymbol{L_+}$ from left on equation (2)

$$\boldsymbol{L_+}\hat{L}_z\psi_{lm} = m\hbar\boldsymbol{L_+}\psi_{lm}$$

As $\boldsymbol{L_+}\hat{L}_z - \hat{L}_z\boldsymbol{L_+} = -\hbar\boldsymbol{L_+}$ which means $\boldsymbol{L_+}\hat{L}_z = \hat{L}_z\boldsymbol{L_+} - \hbar\boldsymbol{L_+}$ use this value in above equation

$$(\hat{L}_z\boldsymbol{L_+} - \hbar\boldsymbol{L_+})\psi_{lm} = m\hbar\boldsymbol{L_+}\psi_{lm}$$

$$\hat{L}_z\boldsymbol{L_+}\psi_{lm} = \hbar\boldsymbol{L_+}\psi_{lm} + m\hbar\boldsymbol{L_+}\psi_{l}$$

$$\hat{L}_z\boldsymbol{L_+}\psi_{lm} = (\boldsymbol{m+1})\hbar\boldsymbol{L_+}\psi_{lm} \text{------- (3)}$$

Now we operate $\boldsymbol{L_+}$ from left on equation (1)

$$\boldsymbol{L_+}\hat{L}^2\psi_{lm} = l(l+1)\hbar^2\boldsymbol{L_+}\psi_{lm}$$

As $\boldsymbol{L_+}\hat{L}^2 - \hat{L}^2\boldsymbol{L_+} = \boldsymbol{0}$ which means $\boldsymbol{L_+}\hat{L}^2 = \hat{L}^2\boldsymbol{L_+}$ **use this value in above equation**

$$\hat{L}^2\boldsymbol{L_+}\psi_{lm} = l(l+1)\hbar^2\boldsymbol{L_+}\psi_{lm} \text{-------- (4)}$$

From equation 3 and 4 we see that $\boldsymbol{L_+}$ **increases the value of m by 1 while** l **remains same.**

So we can write

$$\boldsymbol{L_+}\psi_{lm} = A\psi_{(l,m+1)} \text{----- (5)}$$

Similarly

$$\boldsymbol{L_-}\psi_{lm} = A\psi_{(l,m-1)} \text{------- (6)}$$

Take complex conjugate

$$\boldsymbol{L_+}^*\psi^*{}_{lm} = A^*\psi^*{}_{(l,m+1)} \text{------ (7)}$$

Multiply equation 5 and 7 and integrate

$$\int_{-\infty}^{+\infty} \boldsymbol{L_+}^*\psi^*{}_{lm}\boldsymbol{L_+}\psi_{lm}dv = \int_{-\infty}^{+\infty} A^*\psi^*{}_{(l,m+1)}A\psi_{(l,m+1)}dv$$

$$\boldsymbol{L_+}^* = \boldsymbol{L_-}$$

$$\int_{-\infty}^{+\infty} \psi^*{}_{lm} \boldsymbol{L_- L_+} \psi_{lm} dv = \int_{-\infty}^{+\infty} |A|^2 \psi^*{}_{(l,m+1)} \psi_{(l,m+1)} dv$$

$$\int_{-\infty}^{+\infty} \psi^*{}_{lm} \left(\boldsymbol{L^2 - L_z{}^2 - \hbar L_z}\right) \psi_{lm} dv = |A|^2$$

$$|A|^2 = \int_{-\infty}^{+\infty} \psi^*{}_{lm} \left(l(l+1)\hbar^2 - m^2\hbar^2 - m\hbar^2\right) \psi_{lm} dv$$

$$|A|^2 = \left(l(l+1)\hbar^2 - m^2\hbar^2 - m\hbar^2\right)$$

$$A = \sqrt{l(l+1) - m(m+1)}\ \hbar$$

So

$$\boldsymbol{L_+} \psi_{lm} = A \psi_{(l,m+1)}$$

$$\boldsymbol{L_+} \psi_{lm} = \sqrt{l(l+1) - m(m+1)}\ \hbar\ \psi_{(l,m+1)}$$

Similarly

$$\boldsymbol{L_-} \psi_{lm} = A \psi_{(l,m-1)}$$

$$\boldsymbol{L_-} \psi_{lm} = \sqrt{l(l+1) - m(m+1)}\ \hbar\ \psi_{(l,m-1)}$$

In the same way For Spin and total angular momentum we can write

$$\boldsymbol{S_+} \psi_{sm} = \sqrt{s(s+1) - m(m+1)}\ \hbar\ \psi_{(s,m+1)}$$

$$\boldsymbol{S_-} \psi_{sm} = \sqrt{s(s+1) - m(m+1)}\ \hbar\ \psi_{(s,m-1)}$$

$$\boldsymbol{J_+} \psi_{jm} = \sqrt{j(j+1) - m(m+1)}\ \hbar\ \psi_{(j,m+1)}$$

$$\boldsymbol{J_-} \psi_{jm} = \sqrt{j(j+1) - m(m+1)}\ \hbar\ \psi_{(j,m-1)}$$

Matrix elements of Angular momentum

1. Matrix elements of $\hat{L}_z$

We now that

$$\hat{L}_z\psi_{lm} = m\hbar\psi_{lm}$$

In Ket bra notation

$$\hat{L}_z/\psi_{lm} >= m\hbar/\psi_{lm} >= \hat{L}_z/l,m >= m\hbar/l,m >$$

Multiply both sides by $< l', m'/$

$$\langle l', m'|L_z|l, m\rangle = m\hbar\langle l', m'|l, m\rangle$$

$$\langle l', m'|L_z|l, m\rangle = m\hbar\delta_{ll'}\delta_{mm'}$$

These are the Matrix elements of $\hat{L}_z$. Now we draw matrix

We know that if $l = 0$ which means m=0

Matrix will be $\hat{L}_z = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

$l = 1$ which means m=-1,0,1

We can write states as $/1,1 >,/1,0 >,/1,-1 >$

Matrix will be $\hat{L}_z = \begin{pmatrix} \langle 1,1|L_z|1,1\rangle & \langle 1,1|L_z|1,0\rangle & \langle 1,1|L_z|1,-1\rangle \\ \langle 1,0|L_z|1,1\rangle & \langle 1,0|L_z|1,0\rangle & \langle 1,0|L_z|1,-1\rangle \\ \langle 1,-1|L_z|1,1\rangle & \langle 1,-1|L_z|1,0\rangle & \langle 1,-1|L_z|1,-1\rangle \end{pmatrix}$

Now we know $\delta_{ll'} = 1\ when l = l'\ and\ \delta_{mm'} = 1\ when\ m = m'\ otherwise\ 0$

Here $\langle 1,1|L_z|1,1\rangle,\ l = l' = 1\ and\ m = m' = 1$ so

$$\langle l', m'|L_z|l, m\rangle = m\hbar\delta_{ll'}\delta_{mm'} = \hbar$$

$$\hat{L}_z = \begin{pmatrix} \hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\hbar \end{pmatrix}$$

$$\hat{L}_z = \hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

2. Matrix elements of L^2

In Ket bra notation

$$L^2/\psi_{lm} >= l(l+1)\hbar^2/\psi_{lm} >= L^2/l,m >= l(l+1)\hbar^2/l,m >$$

Multiply both sides by $< l', m'/$

$$\langle l', m'|L^2|l, m\rangle = l(l+1)\hbar^2\langle l', m'|l, m\rangle$$

$$\langle l', m'|L^2|l, m\rangle = l(l+1)\hbar^2\delta_{ll'}\delta_{mm'}$$

These are the Matrix elements of L^2 . Now we draw matrix

We know that if $l = 0$ which means m=0

Matrix will be $L^2 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

$l = 1$ which means m=-1,0,1

We can write states as $/1,1>, /1,0>, /1,-1>$ rows and columns $<1,1/, <1,0/, <1,-1/$

Matrix will be $L^2 = \begin{pmatrix} \langle 1,1|L^2|1,1\rangle & \langle 1,1|L^2|1,0\rangle & \langle 1,1|L^2|1,-1\rangle \\ \langle 1,0|L^2|1,1\rangle & \langle 1,0|L^2|1,0\rangle & \langle 1,0|L^2|1,-1\rangle \\ \langle 1,-1|L^2|1,1\rangle & \langle 1,-1|L^2|1,0\rangle & \langle 1,-1|L^2|1,-1\rangle \end{pmatrix}$

Now we know $\delta_{ll'} = 1\ when l = l'\ and\ \delta_{mm'} = 1\ when\ m = m'\ otherwise\ 0$

Here $\langle 1,1|L^2|1,1\rangle,\ l = l' = 1\ and\ m = m' = 1$ so

$$\langle l', m'|L^2|l, m\rangle = l(l+1)\hbar^2\delta_{ll'}\delta_{mm'} = 2\hbar^2$$

$$L^2 = \begin{pmatrix} 2\hbar^2 & 0 & 0 \\ 0 & 2\hbar^2 & 0 \\ 0 & 0 & 2\hbar^2 \end{pmatrix}$$

$$L^2 = 2\hbar^2\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

3. Matrix elements of L_+

In Ket bra notation

$$L_+/\psi_{lm}>= \sqrt{l(l+1) - m(m+1)}\ \hbar/\psi_{lm+1}>= L_+/l, m>= \sqrt{l(l+1) - m(m+1)}\ \hbar/l, m+1>$$

Multiply both sides by $< l', m'/$

$$\langle l', m'|_{L_+}|l, m\rangle = \sqrt{l(l+1) - m(m+1)}\ \hbar\langle l', m'+1|l, m+1\rangle$$

$$\langle l', m'|_{L_+}|l, m\rangle = \sqrt{l(l+1) - m(m+1)}\ \hbar\delta_{ll'}\delta_{mm'+1}$$

These are the Matrix elements of L_+ . Now we draw matrix

We know that if $l = 0$ which means m=0

Matrix will be $L_+ = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

$l = 1$ which means m=-1,0,1

We can write states as $/1,1>,/1,0>,/1,-1>$ rows and columns $<1,1/,<1,0/,<1,-1/$

Matrix will be $L_+ = \begin{pmatrix} \langle 1,1|L_+|1,1\rangle & \langle 1,1|L_+|1,0\rangle & \langle 1,1|L_+|1,-1\rangle \\ \langle 1,0|L_+|1,1\rangle & \langle 1,0|L_+|1,0\rangle & \langle 1,0|L_+|1,-1\rangle \\ \langle 1,-1|L_+|1,1\rangle & \langle 1,-1|L_+|1,0\rangle & \langle 1,-1|L_+|1,-1\rangle \end{pmatrix}$

Now we know $\delta_{ll'} = 1\ when l = l'\ and\ \delta_{mm'} = 1\ when\ m = m' + 1\ \ otherwise\ 0$

Here $\langle 1,1|L_+|1,1\rangle,\ l = l' = 1\ and\ m = 1\ and\ m' + 1 = 2$ so

$$\langle l', m'|L_+|l, m\rangle = \sqrt{l(l+1) - m(m+1)}\,\hbar\delta_{ll'}\delta_{mm'+1} = 0$$

$$L_+ = \begin{pmatrix} 0 & \sqrt{2}\hbar & 0 \\ 0 & 0 & \sqrt{2}\hbar \\ 0 & 0 & 0 \end{pmatrix}$$

$$L_+ = \sqrt{2}\hbar\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}$$

4. Matrix elements of L_-

In Ket bra notation

$$L_-/\psi_{lm}>= \sqrt{l(l+1) - m(m-1)}\,\hbar/\psi_{lm-1}>= L_-/l, m>= \sqrt{l(l+1) - m(m-1)}\,\hbar/l, m-1>$$

Multiply both sides by $< l', m'/$

$$\langle l', m'|L_-|l, m\rangle = \sqrt{l(l+1) - m(m-1)}\,\hbar\langle l', m'-1|l, m-1\rangle$$

$$\langle l', m'|L_-|l, m\rangle = \sqrt{l(l+1) - m(m-1)}\,\hbar\delta_{ll'}\delta_{mm'-1}$$

These are the Matrix elements of L_- . Now we draw matrix

We know that if $l = 0$ which means m=0

Matrix will be $L_- = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

$l = 1$ Which means m=-1,0,1

We can write states as $/1,1>,/1,0>,/1,-1>$ rows and columns $<1,1/,<1,0/,<1,-1/$

Matrix will be $L_- = \begin{pmatrix} \langle 1,1|L_-|1,1\rangle & \langle 1,1|L_-|1,0\rangle & \langle 1,1|L_-|1,-1\rangle \\ \langle 1,0|L_-|1,1\rangle & \langle 1,0|L_-|1,0\rangle & \langle 1,0|L_-|1,-1\rangle \\ \langle 1,-1|L_-|1,1\rangle & \langle 1,-1|L_-|1,0\rangle & \langle 1,-1|L_-|1,-1\rangle \end{pmatrix}$

Now we know $\delta_{ll'} = 1\ whenl = l'\ and\ \delta_{mm'} = 1\ when\ m = m' - 1\ \ otherwise\ 0$

Here $\langle 1,1|L_-|1,1\rangle,\ l = l' = 1\ and\ m = 1\ and\ m' - 1 = 0$ so

$$\langle l', m'|L_-|l, m\rangle = \sqrt{l(l+1) - m(m+1)}\,\hbar\delta_{ll'}\delta_{mm'+1} = 0$$

$$L_- = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \sqrt{2}\hbar \\ 0 & \sqrt{2}\hbar & 0 \end{pmatrix}$$

$$L_- = \sqrt{2}\hbar \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

5. **Matrix elements of L_x**

As we know

$$L_+ = L_x + iL_y \text{ -------- (a)}$$
$$L_- = L_x - iL_y \text{ -------- (b)}$$

Add a and b

$$L_x = \frac{L_+ + L_-}{2}$$

$$L_x = \frac{1}{2}\left\{\begin{pmatrix} 0 & \sqrt{2}\hbar & 0 \\ 0 & 0 & \sqrt{2}\hbar \\ 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \sqrt{2}\hbar \\ 0 & \sqrt{2}\hbar & 0 \end{pmatrix}\right\}$$

$$L_x = \frac{1}{2}\begin{pmatrix} 0 & \sqrt{2}\hbar & 0 \\ 0 & 0 & 2\sqrt{2}\hbar \\ 0 & \sqrt{2}\hbar & 0 \end{pmatrix}$$

6. **Matrix elements of L_y**

Subtract equation a and b we get

$$L_y = \frac{L_+ - L_-}{2i}$$

$$L_y = \frac{1}{2i}\left\{\begin{pmatrix} 0 & \sqrt{2}\hbar & 0 \\ 0 & 0 & \sqrt{2}\hbar \\ 0 & 0 & 0 \end{pmatrix} - \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \sqrt{2}\hbar \\ 0 & \sqrt{2}\hbar & 0 \end{pmatrix}\right\}$$

$$L_y = \frac{1}{2i}\begin{pmatrix} 0 & \sqrt{2}\hbar & 0 \\ 0 & 0 & -2\sqrt{2}\hbar \\ 0 & -\sqrt{2}\hbar & 0 \end{pmatrix}$$

Quantum mechanical harmonic oscillator using Ladder operator

Consider a harmonic oscillator of mass m, vibrating about mean position.

Its Kinetic energy will be

$$T = \frac{p^2}{2m} \quad \text{---------- (1)}$$

And Potential energy will be

$$V = \frac{1}{2}m\omega^2x^2 \quad \text{---------- (2)}$$

Hamiltonian operator will be

$$H = T + V$$

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2$$

Multiply by wave function $/\psi >$

$$H/\psi >= \frac{p^2}{2m}/\psi > + \frac{1}{2}m\omega^2x^2/>$$

$$H/\psi >= \frac{1}{2m}(p^2 + m^2\omega^2x^2)/\psi >$$

$$H/\psi >= \frac{1}{2m}(p - im\omega x)(p + im\omega x)/\psi >$$

As $H/\psi >= E/\psi >$

So

$$\frac{1}{\sqrt{2m}}(p + im\omega x)\frac{1}{\sqrt{2m}}(p - im\omega x)/\psi >= E/\psi >$$

$$a_+a_-/\psi >= E/\psi >$$

Here

$$a_+ = \frac{1}{\sqrt{2m}}(p + im\omega x)$$

And

$$a_- = \frac{1}{\sqrt{2m}}(p - im\omega x)$$

a_+And a_- are ladder operators respectively, called raising and lowering operators. Now we check the behavior of these operators.

Now

$$a_+a_- = \frac{1}{\sqrt{2m}}(p + im\omega x)\frac{1}{\sqrt{2m}}(p - im\omega x)$$

$$a_+a_- = \frac{1}{2m}(p^2 - im\omega px + im\omega xp + m^2\omega^2x^2)$$

$$a_+a_- = \frac{1}{2m}(p^2 - im\omega(px - xp) + m^2\omega^2x^2)$$

$$a_+a_- = \frac{1}{2m}(p^2 + m^2\omega^2x^2 - im\omega[p,x])$$

But $[p,x] = i\hbar$ so

$$a_+a_- = \frac{1}{2m}\left(p^2 + m^2\omega^2x^2 - im\omega(i\hbar)\right)$$

$$a_+a_- = \frac{1}{2m}(p^2 + m^2\omega^2x^2 + m\omega\hbar)$$

$$a_+a_- = \frac{p^2}{2m} + \frac{m^2\omega^2x^2}{2m} + \frac{m\omega\hbar}{2m}$$

$$a_+a_- = \frac{p^2}{2m} + \frac{m\omega^2x^2}{2m} + \frac{\omega\hbar}{2}$$

As $H = \frac{p^2}{2m} + \frac{m\omega^2x^2}{2}$ so

$$a_+a_- = H + \frac{\omega\hbar}{2} \text{ ---------- (1)}$$

So by the action of raising operator energy increased by the factor $\frac{\omega\hbar}{2}$.

In the same way

$$a_-a_+ = \frac{1}{\sqrt{2m}}(p - im\omega x)\frac{1}{\sqrt{2m}}(p + im\omega x)$$

$$a_-a_+ = \frac{1}{2m}(p^2 + im\omega px - im\omega xp + m^2\omega^2x^2)$$

$$a_-a_+ = \frac{1}{2m}(p^2 + im\omega(px - xp) + m^2\omega^2x^2)$$

$$a_-a_+ = \frac{1}{2m}(p^2 + m^2\omega^2x^2 + im\omega[p,x])$$

But $[p, x] = i\hbar$ so

$$a_- a_+ = \frac{1}{2m}\left(p^2 + m^2\omega^2 x^2 + im\omega(i\hbar)\right)$$

$$a_- a_+ = \frac{1}{2m}(p^2 + m^2\omega^2 x^2 - m\omega\hbar)$$

$$a_- a_+ = \frac{p^2}{2m} + \frac{m^2\omega^2 x^2}{2m} - \frac{m\omega\hbar}{2m}$$

$$a_- a_+ = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2m} - \frac{\omega\hbar}{2}$$

As $H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}$ so

$$a_- a_+ = H - \frac{\omega\hbar}{2} \text{ ------ (2)}$$

So by the action of lowering operator energy decreased by the factor $\frac{\omega\hbar}{2}$.

Now by subtracting equation 1 and 2, we have

$$a_+ a_- - a_- a_+ = H + \frac{\omega\hbar}{2} - H + \frac{\omega\hbar}{2}$$

$$a_+ a_- - a_- a_+ = \hbar\,\omega$$

$$[a_+, a_-] = \hbar\,\omega$$

This is the commutation relation of the raising and lowering operators.

Now we apply these operators on the Schrodinger's equation.

As from equation 1

$$a_+ a_- = H + \frac{\omega\hbar}{2}$$

$$H = a_+ a_- - \frac{\omega\hbar}{2}$$

Now Schrodinger's equation is

$$H/\psi >= E/\psi >$$

So $$\left(a_+ a_- - \frac{\omega\hbar}{2}\right)/\psi >= E/\psi >$$

$$\left(a_+a_-/\psi> -\frac{\omega\hbar}{2}/\psi>\right) = E/\psi>$$

Now operate a_+ operator form the right

$$\left(a_+a_- -\frac{\omega\hbar}{2}\right)a_+/\psi >= a_+E/\psi>$$

$$\left(a_+a_-a_+ -\frac{\omega\hbar}{2}a_+\right)/\psi >= Ea_+/\psi>$$

As

$$a_+a_- - a_-a_+ = \hbar\,\omega$$

So

$$a_-a_+ = a_+a_- - \hbar\,\omega$$

So above equation will become

$$\left(a_+(a_+a_- - \hbar\,\omega) -\frac{\omega\hbar}{2}a_+\right)/\psi >= Ea_+/\psi>$$

$$a_+\left(a_+a_- - \hbar\,\omega -\frac{\omega\hbar}{2}\right)/\psi >= Ea_+/\psi>$$

$$a_+\left(a_+a_- -\frac{\omega\hbar}{2}\right)/\psi >= (E+\hbar\,\omega)a_+/\psi>$$

As $\left(a_+a_- -\frac{\omega\hbar}{2}\right) = H$ therefore

$$a_+H/\psi >= (E+\hbar\,\omega)a_+/\psi>$$

So raising operator a_+ has increased the energy $E$to $E+\hbar\,\omega$.

In the same way we apply lowering operator a_- on Schrodinger's equation.

Now Schrodinger's equation is

As from equation 2

$$a_-a_+ = H - \frac{\omega\hbar}{2}$$

$$H = a_-a_+ + \frac{\omega\hbar}{2}$$

Now Schrodinger's equation is

$$H/\psi >= E/\psi>$$

So $$\left(a_- a_+ + \frac{\omega\hbar}{2}\right)/\psi >= E/\psi >$$

$$\left(a_- a_+/\psi > + \frac{\omega\hbar}{2}/\psi >\right) = E/\psi >$$

Now operate a_- operator form the right

$$\left(a_- a_+ + \frac{\omega\hbar}{2}\right) a_-/\psi >= a_- E/\psi >$$

$$\left(a_- a_+ a_- + \frac{\omega\hbar}{2} a_-\right)/\psi >= E a_-/\psi >$$

As

$$a_+ a_- - a_- a_+ = \hbar\,\omega$$

So

$$a_+ a_- = a_- a_+ + \hbar\,\omega$$

So above equation will become

$$\left(a_-(a_- a_+ + \hbar\,\omega) + \frac{\omega\hbar}{2} a_-\right)/\psi >= E a_-/\psi >$$

$$a_-\left(a_- a_+ + \hbar\,\omega + \frac{\omega\hbar}{2}\right)/\psi >= E a_-/\psi >$$

$$a_-\left(a_- a_+ + \frac{\omega\hbar}{2}\right)/\psi >= (E - \hbar\,\omega) a_-/\psi >$$

As$\left(a_- a_+ + \frac{\omega\hbar}{2}\right) = H$therefore

$$a_- H/\psi >= (E - \hbar\,\omega) a_-/\psi >$$

So raising operator a_- has decreased the energy $E$to $E - \hbar\,\omega$.

Energy Eigen values

Now Schrodinger's equation is

$$H/\psi >= E/\psi >$$

As

$$H = a_- a_+ + \frac{\omega\hbar}{2}$$

First we find the ground state energy that is is the lowest possible energy.

Now for ground state Schrodinger's equation will be

$$H/\psi_o >= E_o/\psi_o >$$

So $$\left(a_- a_+ + \frac{\omega\hbar}{2}\right)/\psi_o >= E_o/\psi_o >$$

We define a new operator N such that $N = a_- a_+$

And $N/\psi >= n\omega\hbar$ so above equation will become

$$\left(N + \frac{\omega\hbar}{2}\right)/\psi >= E/\psi >$$

$$\left(n\omega\hbar + \frac{\omega\hbar}{2}\right)/\psi >= E/>$$

Put $E = E_n$ so

$$\left(n\omega\hbar + \frac{\omega\hbar}{2}\right)/\psi >= E_n/\psi >$$

$$E_n = \left(n\omega\hbar + \frac{\omega\hbar}{2}\right)$$

$$E_n = \left(n + \frac{1}{2}\right)\omega\hbar$$

This is the energy Eigen values of the harmonic oscillator.

Here $n = 0,1,2,3, \ldots \ldots$

Wave function of the harmonic oscillator

If we apply lowering operator a_- to lowest possible state$/\psi_0 >$, we get zero i.e

$$a_-/\psi_0 >= 0$$

$$\frac{1}{\sqrt{2m}}(p - im\omega x)/\psi_0 >= 0$$

$$p/\psi_0 > -im\omega x/\psi_0 >= 0$$

But $p = -i\hbar\frac{d}{dx}$ so

$$-i\hbar\frac{d}{dx}/\psi_0 > -im\omega x/\psi_0 >= 0$$

$$\hbar \frac{d}{dx} /\psi_0 >= -m\omega x/\psi_0 >$$

$$\frac{d/\psi_0 >}{/\psi_0 >} = \frac{-m\omega x}{\hbar} dx$$

Integrate both sides

$$\int \frac{d/\psi_0 >}{/\psi_0 >} = \int \frac{-m\omega x}{\hbar} dx$$

$$\ln /\psi_0 > = \frac{-m\omega x^2}{2\hbar} + \ln A$$

$$\ln /\psi_0 > - \ln A = \frac{-m\omega x^2}{2\hbar}$$

$$\ln \frac{/\psi_0 >}{A} = \frac{-m\omega x^2}{2\hbar}$$

$$\frac{/\psi_0 >}{A} = e^{\frac{-m\omega x^2}{2\hbar}}$$

$$/\psi_0 >= Ae^{\frac{-m\omega x^2}{2\hbar}}$$

Put $\alpha = \frac{m\omega}{\hbar}$ we have

$$/\psi_0 >= Ae^{\frac{-\alpha x^2}{2}}$$

This is the ground state wave function. By applying normalized condition we have

$$A = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}$$

So normalized wave function will be

$$/\psi_0 >= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{\frac{-\alpha x^2}{2}}$$

Spin Angular momentum

Introduction

In 1920, Otto Stern and Walter Gerlach designed an experiment, which unintentionally led to the discovery that electrons have their own individual, continuous spin even as they move along their orbital of an atom. Today, this electron spin is indicated by the fourth quantum number, also known as the Electron Spin Quantum Number and denoted by m_s. In 1925, Samuel Goudsmit and George Uhlenbeck made the claim that features of the hydrogen spectrum that were unexamined might by explained by assuming electrons act as if it has a spin. This spin can be denoted by an arrow pointing up, which is +1/2, or an arrow pointing down, which is -1/2.

The experiment mentioned above by Otto Stern and Walter Gerlach was done with silver which was put in an oven and vaporized. The result was that silver atoms formed a beam that passed through a magnetic field in which it split in two.

An explanation of this is that an electron has a magnetic field due to its spin. When electrons that have opposite spins are put together, there is no net magnetic field because the positive and negative spins cancel each other out. The silver atom used in the experiment has a total of 47 electrons, 23 of one spin type, and 24 of the opposite. Because electrons of the same spin cancel each other out, the one unpaired electron in the atom will determine the spin. There is a high likelihood for either spin due to the large number of electrons, so when it went through the magnetic field it split into two beams.

Brief Explanation of Quantum Numbers

Note: In this module, capital "L" will be used instead of small case "l" for angular momentum quantum number.

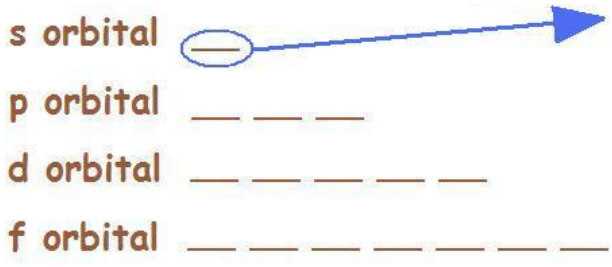
A total of four quantum numbers were developed to better understand the movement and pathway of electrons in its designated orbital within an atom.

Principal quantum number (n): energy level n = 1, 2, 3, 4, ...

Orbital Angular Momentum Quantum Number (L): shape (of orbital) L = 0, 1, 2, 3, ...n-1

Magnetic Quantum Number (m_L): orientation m_L = interval of (-L, +L)

Electron Spin Quantum Number (m_s): independent of other three quantum numbers because m_s is always = –½ or +½

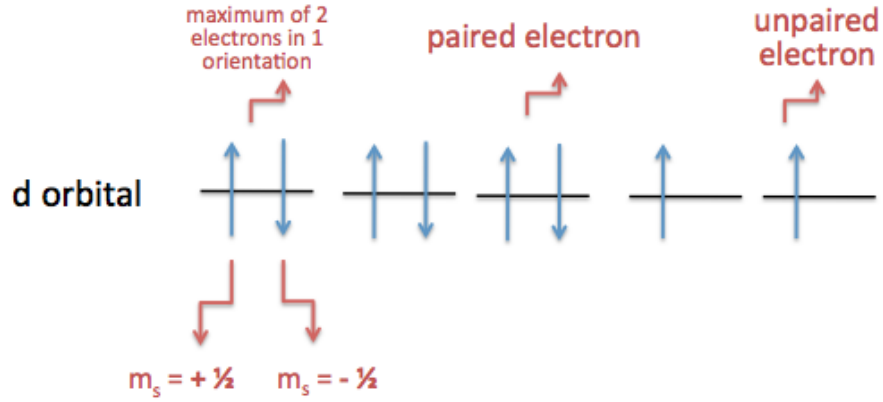


The lines represent how many orientations each orbital has, (e.g. the s-orbital has one orientation, a p-orbital has three orientations, etc.) and each line can hold up to two electrons, represented by up and down arrows. An electron with an up arrow means it has an electron spin of +1212, and an electron with a down arrow means it has an electron spin of -1212.

Electron Spin

Significance: Although the electron spin is limited to +½ or –½, certain rules apply when assigning electrons of different spins to fill a subshell (orientations of an orbital) .

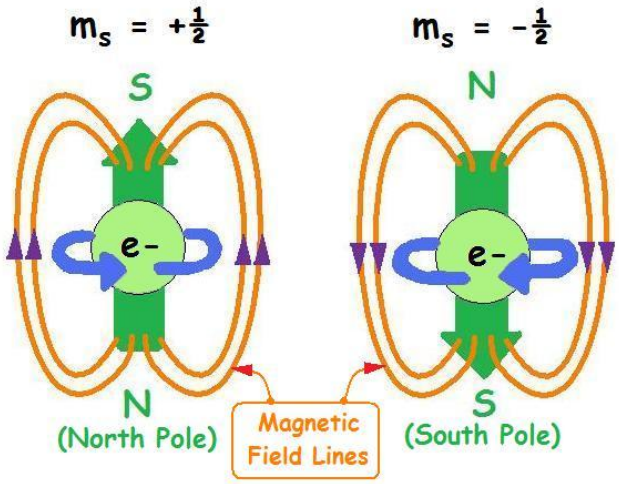
Example :



This is **paramagnetic** because there exists one or more unpaired electrons.

An atom with unpaired electrons are termed as paramagnetic results in a net magnetic field because electrons within the orbital are not stabilized or balanced enough atoms are attracted to magnets. An atom with paired electrons are termed as diamagnetic results in no magnetic field because electrons are uniform and stabilized within the orbital atoms are not attracted to magnets Applying concepts of magnetism with liquid nitrogen and liquid oxygen:

The magnetic spin of an electron follows in the direction of the magnetic field lines as shown below.



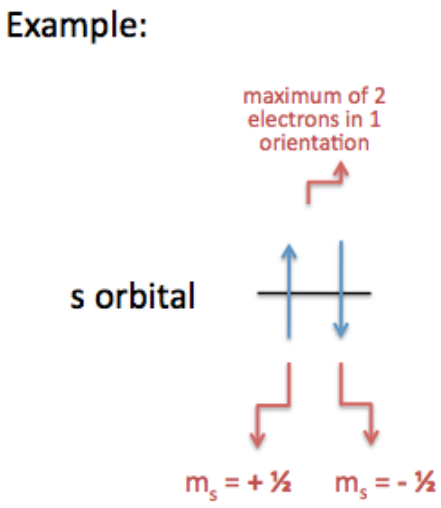
Assigning Spin Direction

An effective visual on how to assign spin directions can be represented by the orbital diagram (shown previously and below.) Restrictions apply when assigning spin directions to electrons, so the following Pauli Exclusion Principle and Hund's Rule help explain this.

When one is filling an orbital, such as the p orbital, you must fill all orbitals possible with one electron spin before assigning the opposite spin. For example, when filling the fluorine, which will have a total of two electrons in the s orbital and a total of five electrons in the p orbital, one will start with the s orbital which will contain two electrons. So, the first electron one assigns will be spin up and the next spin down. Moving on to the three p orbitals that one will start by assigning a spin up electron in each of the three orbitals. That takes up three of the five electrons, so with the remaining two electrons, one returns to the first and second p orbital and assigns the spin down electron. This means there will be one unpaired electron in fluorine so it will be paramagnetic.

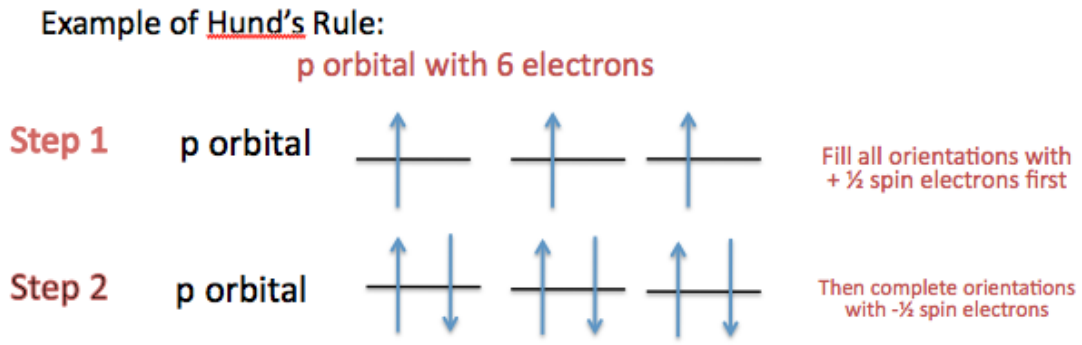
Pauli Exclusion Principle

The Pauli exclusion principle declares that there can only be a maximum of two electrons for every one orientation, and the two electrons must be opposite in spin direction; meaning one electron has ms=+12ms=+12 and the other electron has ms=−12ms=−12.



Hund's Rule

Hund's Rule declares that the electrons in the orbital are filled up first by the +1/2, -1/2 spin. Once all the orbitals are filled with unpaired +1/2, -1/2 spins, the orbitals are then filled with the -1212 spin. (See examples below, labeled electronic configuration.)


Example of Hund's Rule:
p orbital with 6 electrons
Step 1
p orbital
Fill all orientations with + ½ spin electrons first
Step 2
p orbital
Then complete orientations with -½ spin electrons

Identifying Spin Direction

Determine the number of electrons the atom has.

Draw the electron configuration for the atom. See Electronic Configurations for more information.

Distribute the electrons, using up and down arrows to represent the electron spin direction.

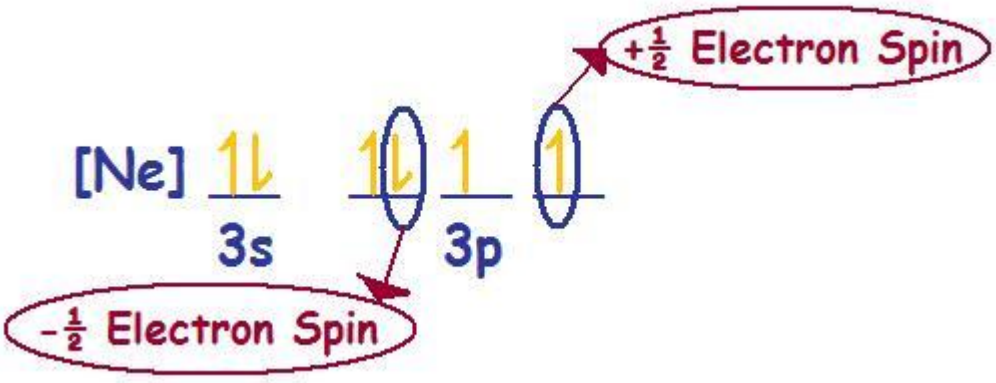
Example 1: Sulfur

Sulfur - S (16 electrons)

Electronic Configuration:

1s2 2s2 2p6 3s2 3p4 OR [Ne] 3s2 3p4

As shown in the following image, this is a demonstration of a -1212 and a +1212 Electron Spin.



Principal Quantum Number & (s, p, d, f) Orbitals

When given a principal quantum number, n, with either the s, p, d or f-orbital, identify all the possibilities of L, m_L and m_s.

Example 2

Given 5f, identify all the possibilities of the four quantum numbers.

Solution

In this problem, the principal quantum number is n = 5 (the subshell number placed in front of the orbital, the f-orbital in this case). Since we are looking at the f-obital, therefore L = 3. (Look under "Subshells" in the module Quantum Numbers for more information) Knowing L = 3, we can interpret that m_L = 0, ±± 1, ±± 2, ±± 3 since m_L = -L,...,-1, 0, 1,...+L. As for m_s, since it isn't specified in the problem as to whether it is -1212 or +1212, therefore for this problem, it could be both; meaning that the electron spin quantum number is ±±1212.

Example 3

Given 6s and m_L= +1, identify all the possibilities of the four quantum numbers.

Solution

n	L	m_L	m_s

The principal quantum number is n = 6. Looking at the s-orbital, we know that L = 0. Knowing that m_L = -L,...,-1, 0, 1,...+L, therefore m_L = +1 is **not possible** since in this problem, the interval of m_L can only equal to 0 according to the angular momentum quantum number, L.

Example 4

Given 4d and m_s = +1212, identify all the possibilities of the four quantum numbers.

Solution

The principal quantum number is n = 4. Given that it is a d-orbital, we know that L = 2. Therefore, m_L = 0, ±± 1, ±± 2 since m_L = -L,...,-1, 0, 1,...+L. For m_s, this problem specifically said m_s = +1212; meaning that the electron spin quantum number is +1212.

Electron Spin: Where to begin?

First, draw a table labeled n, L, $m_L$and m_s, as shown below:

Then, depending on what the question is asking for, fill in the boxes accordingly. Finally, determine the number of electrons for the given quantum number, n, with regards to L, m_L and m_s.

Example 5

How many electrons can have n = 5 and L = 1? 6

n	L	m_L	m_s
5	1	-1	-1212 , +1212
		0	
		+1	

This problem includes both -1212 , +1212 , therefore the answer is **6** electrons based on the m_L.

Example 6

How many electrons can have n = 5 and m_s = -1212? 5

n	L	m_L
5	4	±± 4
	3	±± 3
	2	±± 2

	1	±± 1	
	0	0	

This problem only wants the Spin Quantum Number to be -1212 , the answer is **5** electrons based on the m_L.

Example 7

How many electrons can have n = 3, L = 2 and m_L = 3? zero

Solution

n	L	m_L
3	2	NOT POSSIBLE

Since **m_L = -L...-1, 0, +1...+L** (See Electronic Orbitals for more information), m_L is not possible because L = 2, so it is impossible for m_L to be equal to 3. So, there is **zero** electrons.

Example 8

How many electrons can have n = 3, m_L = +2 and m_s = +1212? 1

Solution

n	L	m_L	
3	2	-2, +2	
	1	±± 1	
	0	0	

This problem only wants the Spin Quantum Number to be +1212 , the answer is **1** electrons based on the m_L.

Commutation relations of Spin angular Momentum

1. $[S_x, S_y] = i\hbar S_z$
2. $[S_y, S_z] = i\hbar S_x$
3. $[S_z, S_x] = i\hbar S_y$

Derivation

1. $[S_x, S_y] = S_x S_y - S_y S_x$
   As in Matrix form

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

So

$$[S_x, S_y] = \frac{\hbar^2}{4}\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \frac{\hbar^2}{4}\begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$$

$$[S_x, S_y] = \frac{\hbar^2}{4}\begin{pmatrix} 2i & 0 \\ 0 & -2i \end{pmatrix}$$

$$[S_x, S_y] = 2i\frac{\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$[S_x, S_y] = i\hbar\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$[S_x, S_y] = i\hbar S_z$$

2. $[S_y, S_z] = S_y S_z - S_z S_y$

$$[S_y, S_z] = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$[S_y, S_z] = \frac{\hbar^2}{4}\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} - \frac{\hbar^2}{4}\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$$

$$[S_y, S_z] = \frac{\hbar^2}{4}\begin{pmatrix} 0 & 2i \\ 2i & 0 \end{pmatrix}$$

$$[S_y, S_z] = 2i\frac{\hbar^2}{4}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$[S_y, S_z] = i\hbar\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$[S_y, S_z] = i\hbar S_x$$

3. $[S_z, S_x] = S_z S_x - S_x S_z$

$$[S_z, S_x] = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$[S_z, S_x] = \frac{\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - \frac{\hbar^2}{4}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$[S_z, S_x] = \frac{\hbar^2}{4}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} - \frac{\hbar^2}{4}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$

$$[S_z, S_x] = \frac{\hbar^2}{4}\begin{pmatrix} 0 & 2 \\ -2 & 0 \end{pmatrix}$$

$$[S_z, S_x] = -2\hbar\frac{\hbar}{4}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$

$$[S_z, S_x] = i\hbar\frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$[S_z, S_x] = i\hbar S_y$$

Prove that

1. ${S_x}^2 = {S_y}^2 = {S_z}^2 = \frac{\hbar^2}{4}I$

2. $S^2 = \frac{3\hbar^2}{4} I$

   1. $S_x{}^2 = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} = \frac{\hbar^2}{4}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} = \frac{\hbar^2}{4} I$ in the same way $S_y{}^2 = S_z{}^2 = \frac{\hbar^2}{4} I$
   2. $S^2 = S_x{}^2 + S_y{}^2 + S_z{}^2 = \frac{\hbar^2}{4} I + \frac{\hbar^2}{4} I + \frac{\hbar^2}{4} I = \frac{3\hbar^2}{4} I$

Paulli,s Spin Matrices

Like angular momentum operator L, Spin angular momentum operator S can also be written as

$$\boldsymbol{S}_+ \psi_{sm} = \sqrt{s(s+1) - m(m+1)}\ \hbar\ \psi_{(s,m+1)} \text{-------- (1)}$$

$$\boldsymbol{S}_- \psi_{sm} = \sqrt{s(s+1) - m(m-1)}\ \hbar\ \psi_{(s,m-1)} \text{---------- (2)}$$

$$\hat{S}^2 \psi_{lm} = s(s+1)\hbar^2 \psi_{sm} \text{------ (3)}$$

$$\hat{S}_z \psi_{sm} = m\hbar\psi_{sm} \text{ ------- (4)}$$

Here $s = \frac{1}{2}\ and\ m = -s\ to + s$

Now we take equation (1)

$$\boldsymbol{S}_+ \psi_{sm} = \sqrt{s(s+1) - m(m+1)}\ \hbar\ \psi_{(s,m+1)}$$

in ket bra notation

$$\boldsymbol{S}_+ / s, m >= \sqrt{s(s+1) - m(m+1)}\ \hbar\ / s, m+1 >$$

Multiply by **<s',m'/** from left

$$< \mathbf{s}', \mathbf{m}' / \boldsymbol{S}_+ / s, m >= \sqrt{s'(s'+1) - m'(m'+1)}\ \hbar\ < s', m' / s, m+1 >$$

$$< \mathbf{s}', \mathbf{m}' / \boldsymbol{S}_+ / s, m >= \sqrt{s'(s'+1) - m'(m'+1)}\ \hbar\ \delta_{ss'} \delta_{mm'+1}$$

These are the Matrix elements of $\boldsymbol{S}_+$. Now we draw matrix

We know that if $s = \frac{1}{2}$ which means m=1/2,-1/2

We can write states as $/\frac{1}{2}, \frac{1}{2}>$, $/\frac{1}{2}, \frac{-1}{2}>$ rows and columns $<\frac{1}{2}, \frac{1}{2}/, <\frac{1}{2}, \frac{-1}{2}/$

Matrix will be $\boldsymbol{S}_+ = \begin{pmatrix} \left\langle \frac{1}{2}, \frac{1}{2} \middle| \boldsymbol{S}_+ \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle \frac{1}{2}, \frac{1}{2} \middle| \boldsymbol{S}_+ \middle| \frac{1}{2}, \frac{-1}{2} \right\rangle \\ \left\langle \frac{1}{2}, \frac{-1}{2} \middle| \boldsymbol{S}_+ \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle \frac{1}{2}, \frac{-1}{2} \middle| \boldsymbol{S}_+ \middle| \frac{1}{2}, \frac{-1}{2} \right\rangle \end{pmatrix}$

Now we know $\delta_{ss'} = 1\ whens = s'\ and\ \delta_{mm'} = 1\ when\ m = m' + 1\ \ otherwise\ 0$

Here $\left\langle \frac{1}{2},\frac{1}{2}\middle|\boldsymbol{S}_{+}\middle|\frac{1}{2},\frac{1}{2}\right\rangle$, $s=s'=\frac{1}{2}\ and\ m=\frac{1}{2}\ and\ m'+1=\frac{1}{2}+1=\frac{3}{2}$ so

$$<\mathbf{s}',\mathbf{m}'/\boldsymbol{S}_{+}/s,m>=\sqrt{s'(s'+1)-m'(m'+1)}\ \hbar\ \delta_{ss'}\delta_{mm'+1}=0$$

Here $\left\langle \frac{1}{2},\frac{1}{2}\middle|\boldsymbol{S}_{+}\middle|\frac{1}{2},\frac{-1}{2}\right\rangle$, $s=s'=\frac{1}{2}\ and\ m=\frac{-1}{2}\ and\ m'+1=\frac{1}{2}+1=\frac{3}{2}$ so

$$<\mathbf{s}',\mathbf{m}'/\boldsymbol{S}_{+}/s,m>=\sqrt{s'(s'+1)-m'(m'+1)}\ \hbar\ \delta_{ss'}\delta_{mm'+1}=0$$

Here $\left\langle \frac{1}{2},\frac{-1}{2}\middle|\boldsymbol{S}_{+}\middle|\frac{1}{2},\frac{1}{2}\right\rangle$, $s=s'=\frac{1}{2}\ and\ m=\frac{1}{2}\ and\ m'+1=\frac{-1}{2}+1=\frac{1}{2}$ so

$$<\mathbf{s}',\mathbf{m}'/\boldsymbol{S}_{+}/s,m>=\sqrt{s'(s'+1)-m'(m'+1)}\ \hbar\ \delta_{ss'}\delta_{mm'+1}=\hbar$$

Here $\left\langle \frac{1}{2},\frac{-1}{2}\middle|\boldsymbol{S}_{+}\middle|\frac{1}{2},\frac{-1}{2}\right\rangle$, $s=s'=\frac{1}{2}\ and\ m=\frac{-1}{2}\ and\ m'+1=\frac{-1}{2}+1=\frac{1}{2}$ so

$$<\mathbf{s}',\mathbf{m}'/\boldsymbol{S}_{+}/s,m>=\sqrt{s'(s'+1)-m'(m'+1)}\ \hbar\ \delta_{ss'}\delta_{mm'+1}=0$$

$$\boldsymbol{S}_{+}=\begin{pmatrix}0 & 0\\ \hbar & 0\end{pmatrix}$$

Now we take equation (2)

$$\boldsymbol{S}_{-}\psi_{sm}=\sqrt{s(s+1)-m(m-1)}\ \hbar\ \psi_{(s,m-1)}$$

in ket bra notation

$$\boldsymbol{S}_{-}/s,m>=\sqrt{s(s+1)-m(m-1)}\ \hbar\ /s,m-1>$$

Multiply by **<s',m'/** from left

$$<\mathbf{s}',\mathbf{m}'/\boldsymbol{S}_{-}/s,m>=\sqrt{s'(s'+1)-m'(m'-1)}\ \hbar\ <s',m'/s,m-1>$$

$$<\mathbf{s}',\mathbf{m}'/\boldsymbol{S}_{-}/s,m>=\sqrt{s'(s'+1)-m'(m'-1)}\ \hbar\ \delta_{ss'}\delta_{mm'-1}$$

These are the Matrix elements of $\boldsymbol{S}_{-}$. Now we draw matrix

We know that if $s=\frac{1}{2}$ which means m=1/2,-1/2

We can write states as $/\frac{1}{2},\frac{1}{2}>$, $/\frac{1}{2},\frac{-1}{2}>$ rows and columns $<\frac{1}{2},\frac{1}{2}/,<\frac{1}{2},\frac{-1}{2}/$

Matrix will be $\boldsymbol{S}_{-}=\begin{pmatrix}\left\langle \frac{1}{2},\frac{1}{2}\middle|\boldsymbol{S}_{-}\middle|\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle \frac{1}{2},\frac{1}{2}\middle|\boldsymbol{S}_{-}\middle|\frac{1}{2},\frac{-1}{2}\right\rangle\\ \left\langle \frac{1}{2},\frac{-1}{2}\middle|\boldsymbol{S}_{-}\middle|\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle \frac{1}{2},\frac{-1}{2}\middle|\boldsymbol{S}_{-}\middle|\frac{1}{2},\frac{-1}{2}\right\rangle\end{pmatrix}$

Now we know $\delta_{ss'} = 1\ whens = s'\ and\ \delta_{mm'} = 1\ when\ m = m' - 1\ \ otherwise\ 0$

Here $\left\langle \frac{1}{2},\frac{1}{2}\middle|\boldsymbol{S}_-\middle|\frac{1}{2},\frac{1}{2}\right\rangle,\ s = s' = \frac{1}{2}\ and\ m = \frac{1}{2}\ and\ m' - 1 = \frac{1}{2} - 1 = \frac{-1}{2}$ so

$$< \mathbf{s}', \mathbf{m}'/\boldsymbol{S}_-/s, m >= \sqrt{s'(s'+1) - m'(m'-1)}\ \hbar\ \delta_{ss'}\delta_{mm'-1} = 0$$

Here $\left\langle \frac{1}{2},\frac{1}{2}\middle|\boldsymbol{S}_-\middle|\frac{1}{2},\frac{-1}{2}\right\rangle,\ s = s' = \frac{1}{2}\ and\ m = \frac{-1}{2}\ and\ m' - 1 = \frac{1}{2} - 1 = \frac{-1}{2}$ so

$$< \mathbf{s}', \mathbf{m}'/\boldsymbol{S}_-/s, m >= \sqrt{s'(s'+1) - m'(m'-1)}\ \hbar\ \delta_{ss'}\delta_{mm'-1} = \hbar$$

Here $\left\langle \frac{1}{2},\frac{-1}{2}\middle|\boldsymbol{S}_-\middle|\frac{1}{2},\frac{1}{2}\right\rangle,\ s = s' = \frac{1}{2}\ and\ m = \frac{1}{2}\ and\ m' - 1 = \frac{-1}{2} - 1 = \frac{-3}{2}$ so

$$< \mathbf{s}', \mathbf{m}'/\boldsymbol{S}_-/s, m >= \sqrt{s'(s'+1) - m'(m'-1)}\ \hbar\ \delta_{ss'}\delta_{mm'-1} = 0$$

Here $\left\langle \frac{1}{2},\frac{-1}{2}\middle|\boldsymbol{S}_-\middle|\frac{1}{2},\frac{-1}{2}\right\rangle,\ s = s' = \frac{1}{2}\ and\ m = \frac{-1}{2}\ and\ m' - 1 = \frac{-1}{2} - 1 = \frac{-3}{2}$ so

$$< \mathbf{s}', \mathbf{m}'/\boldsymbol{S}_-/s, m >= \sqrt{s'(s'+1) - m'(m'-1)}\ \hbar\ \delta_{ss'}\delta_{mm'-1} = 0$$

$$\boldsymbol{S}_- = \begin{pmatrix} 0 & \hbar \\ 0 & 0 \end{pmatrix}$$

Now as

$$\boldsymbol{S}_+ = \mathbf{S_x} + \mathbf{iS_y}\ \text{-------(a)}$$

$$\boldsymbol{S}_- = \mathbf{S_x} - \mathbf{iS_y}\text{-------(b)}$$

Add and subtract equations a and b we get

$$\mathbf{S_x} = \frac{\boldsymbol{S}_+ + \boldsymbol{S}_-}{\mathbf{2}}\text{--------(c)}$$

$$\mathbf{S_y} = \frac{\boldsymbol{S}_+ - \boldsymbol{S}_-}{\mathbf{2i}}\text{--------(d)}$$

Now

$$\mathbf{S_x} = \frac{\begin{pmatrix} 0 & 0 \\ \hbar & 0 \end{pmatrix} + \begin{pmatrix} 0 & \hbar \\ 0 & 0 \end{pmatrix}}{\mathbf{2}}$$

$$\mathbf{S_x} = \frac{\mathbf{1}}{\mathbf{2}}\begin{pmatrix} 0 & \hbar \\ \hbar & 0 \end{pmatrix} = \frac{\hbar}{\mathbf{2}}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Similarly

$$\mathbf{S_y} = \frac{\boldsymbol{S}_+ - \boldsymbol{S}_-}{\mathbf{2i}} = \frac{\begin{pmatrix} 0 & 0 \\ \hbar & 0 \end{pmatrix} - \begin{pmatrix} 0 & \hbar \\ 0 & 0 \end{pmatrix}}{\mathbf{2i}} = \frac{\begin{pmatrix} 0 & -\hbar \\ \hbar & 0 \end{pmatrix}}{\mathbf{2}}$$

$$\mathbf{S_y} = \frac{\hbar}{\mathbf{2}}\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$$

1. Now Matrix elements of $\hat{S}_z$

We now that

$$\hat{S}_z\psi_{sm} = m\hbar\psi_{sm}$$

In Ket bra notation

$$\hat{S}_z\psi_{sm} >= m\hbar/\psi_{sm} >= \hat{S}_z/s,m >= m\hbar/s,m >$$

Multiply both sides by $< s', m'/$

$$\langle s', m'|\hat{S}_z|s, m\rangle = m\hbar\langle s', m'|s, m\rangle$$

$$\langle s', m'|\hat{S}_z|s, m\rangle = m\hbar\delta_{ss'}\delta_{mm'}$$

These are the Matrix elements of $\hat{S}_z$. Now we draw matrix

$s = \frac{1}{2}$ which means m=1/2 , -1/2

We can write states as $/\frac{1}{2},\frac{1}{2}>,/\frac{1}{2},\frac{-1}{2}>$ $colmns\ and\ rows$ $<\frac{1}{2},\frac{1}{2}/,<\frac{1}{2},\frac{-1}{2}/$

Matrix will be $S_z = \begin{pmatrix} \left\langle \frac{1}{2},\frac{1}{2}\middle|S_z\middle|\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle \frac{1}{2},\frac{1}{2}\middle|S_z\middle|\frac{1}{2},\frac{-1}{2}\right\rangle \\ \left\langle \frac{1}{2},\frac{-1}{2}\middle|S_z\middle|\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle \frac{1}{2},\frac{-1}{2}\middle|S_z\middle|\frac{1}{2},\frac{-1}{2}\right\rangle \end{pmatrix}$

Now we know $\delta_{ss'} = 1\ when\ s = s'\ and\ \delta_{mm'} = 1\ when\ m = m'\ otherwise\ 0$

Here $\left\langle \frac{1}{2},\frac{1}{2}\middle|S_z\middle|\frac{1}{2},\frac{1}{2}\right\rangle,\ s = s' = \frac{1}{2}\ and\ m = m' = \frac{1}{2}$ so

$$\langle s', m'|\hat{S}_z|s, m\rangle = m\hbar\delta_{ss'}\delta_{mm'} = \frac{\hbar}{2}$$

Here $\left\langle \frac{1}{2},\frac{1}{2}\middle|S_z\middle|\frac{1}{2},\frac{-1}{2}\right\rangle,\ s = s' = \frac{1}{2}\ and\ m = \frac{-1}{2}\ m' = \frac{1}{2}$ so

$$\langle s', m'|\hat{S}_z|s, m\rangle = m\hbar\delta_{ss'}\delta_{mm'} = 0$$

Here $\left\langle \frac{1}{2},\frac{-1}{2}\middle|S_z\middle|\frac{1}{2},\frac{1}{2}\right\rangle,\ s = s' = \frac{1}{2}\ and\ m = \frac{1}{2}m' = \frac{-1}{2}$ so

$$\langle s', m'|\hat{S}_z|s, m\rangle = m\hbar\delta_{ss'}\delta_{mm'} = 0$$

Here $\left\langle \frac{1}{2},\frac{-1}{2}\middle|S_z\middle|\frac{1}{2},\frac{-1}{2}\right\rangle,\ s = s' = \frac{1}{2}\ and\ m = m' = \frac{-1}{2}$ so

$$\langle s', m'|\hat{S}_z|s, m\rangle = m\hbar\delta_{ss'}\delta_{mm'} = \frac{-\hbar}{2}$$

$$S_z = \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & \frac{-\hbar}{2} \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

2. Matrix elements of S^2

In Ket bra notation

$$S^2/\psi_{sm} >= s(s+1)\hbar^2/\psi_{sm} >= S^2/s,m >= s(s+1)\hbar^2/s,m >$$

Multiply both sides by $< s', m'/$

$$\langle s', m'|S^2|s,m\rangle = s(s+1)\hbar^2\langle s', m'|s,m\rangle$$

$$\langle s', m'|S^2|s,m\rangle = s(s+1)\hbar^2\delta_{ss'}\delta_{mm'}$$

These are the Matrix elements of S^2 . Now we draw matrix

We know that if $s = \frac{1}{2}$ which means m=1/2 , -1/2

We can write states as $/\frac{1}{2},\frac{1}{2}>,/\frac{1}{2},\frac{-1}{2}>$ $colmns\ and\ rows$ $<\frac{1}{2},\frac{1}{2}/,<\frac{1}{2},\frac{-1}{2}/$

Matrix will be $S^2 = \begin{pmatrix} \left\langle \frac{1}{2},\frac{1}{2}\middle|S^2\middle|\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle \frac{1}{2},\frac{1}{2}\middle|S^2\middle|\frac{1}{2},\frac{-1}{2}\right\rangle \\ \left\langle \frac{1}{2},\frac{-1}{2}\middle|S^2\middle|\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle \frac{1}{2},\frac{-1}{2}\middle|S^2\middle|\frac{1}{2},\frac{-1}{2}\right\rangle \end{pmatrix}$

Now we know $\delta_{ss'} = 1\ when\ s = s'\ and\ \delta_{mm'} = 1\ when\ m = m'\ otherwise\ 0$

Here $\left\langle \frac{1}{2},\frac{1}{2}\middle|S^2\middle|\frac{1}{2},\frac{1}{2}\right\rangle,\ s = s' = \frac{1}{2}\ and\ m = m' = \frac{1}{2}$ so

$$\langle s', m'|S^2|s,m\rangle = s(s+1)\hbar^2\delta_{ss'}\delta_{mm'} = \frac{3\hbar^2}{4}$$

Here $\left\langle \frac{1}{2},\frac{1}{2}\middle|S_z\middle|\frac{1}{2},\frac{-1}{2}\right\rangle,\ s = s' = \frac{1}{2}\ and\ m = \frac{-1}{2}\ m' = \frac{1}{2}$ so

$$\langle s', m'|S^2|s,m\rangle = s(s+1)\hbar^2\delta_{ss'}\delta_{mm'} = 0$$

Here $\left\langle \frac{1}{2},\frac{-1}{2}\middle|S_z\middle|\frac{1}{2},\frac{1}{2}\right\rangle,\ s = s' = \frac{1}{2}\ and\ m = \frac{1}{2}m' = \frac{-1}{2}$ so

$$\langle s', m'|S^2|s,m\rangle = s(s+1)\hbar^2\delta_{ss'}\delta_{mm'} = 0$$

Here $\left\langle \frac{1}{2},\frac{-1}{2}\middle|S^2\middle|\frac{1}{2},\frac{-1}{2}\right\rangle,\ s = s' = \frac{1}{2}\ and\ m = m' = \frac{-1}{2}$ so

$$\langle s', m'|S^2|s,m\rangle = s(s+1)\hbar^2\delta_{ss'}\delta_{mm'} = \frac{3\hbar^2}{4}$$

$$S^2 = \begin{pmatrix} \frac{3\hbar^2}{4} & 0 \\ 0 & \frac{3\hbar^2}{4} \end{pmatrix} = \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Now we re -write $\mathbf{S_x}, \mathbf{S_y}, \mathbf{S_z}$

$$\mathbf{S_x} = \frac{\hbar}{\mathbf{2}}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar}{\mathbf{2}}\boldsymbol{\sigma_x}$$

$$\mathbf{S_y} = \frac{\hbar}{\mathbf{2}}\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} = \frac{\hbar}{\mathbf{2}}\boldsymbol{\sigma_y}$$

$$S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{\mathbf{2}}\boldsymbol{\sigma_z}$$

Here

$$\boldsymbol{\sigma_x} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \boldsymbol{\sigma_y} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \boldsymbol{\sigma_z} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Are called paulli,s spin matrices.

Commutation Relations of Puali Spin matrices

1. $\left[\boldsymbol{\sigma_x}, \boldsymbol{\sigma_y}\right] = \mathbf{2}\boldsymbol{i}\boldsymbol{\sigma_z}$

2. $\left[\boldsymbol{\sigma_y}, \boldsymbol{\sigma_z}\right] = \mathbf{2}\boldsymbol{i}\boldsymbol{\sigma_x}$

3. $\left[\boldsymbol{\sigma_z}, \boldsymbol{\sigma_x}\right] = \mathbf{2}\boldsymbol{i}\boldsymbol{\sigma_y}$

$$\left[\boldsymbol{\sigma_x}, \boldsymbol{\sigma_y}\right] = \boldsymbol{\sigma_x}\boldsymbol{\sigma_y} - \boldsymbol{\sigma_y}\boldsymbol{\sigma_x}$$

$$\left[\boldsymbol{\sigma_x}, \boldsymbol{\sigma_y}\right] = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\left[\boldsymbol{\sigma_x}, \boldsymbol{\sigma_y}\right] = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = \begin{pmatrix} 2i & 0 \\ 0 & -2i \end{pmatrix}$$

$$\left[\boldsymbol{\sigma_x}, \boldsymbol{\sigma_y}\right] = 2i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = 2i\boldsymbol{\sigma_z}$$

Similarly 2 and 3.

Now we have to show that Pauli spin matrices are anti commute. That is

1. $\left\{\boldsymbol{\sigma_x}, \boldsymbol{\sigma_y}\right\} = 0$ Here **{ }** are called anti-commute brackets.
2. $\left\{\boldsymbol{\sigma_y}, \boldsymbol{\sigma_z}\right\} = 0$
3. $\{\boldsymbol{\sigma_z}, \boldsymbol{\sigma_x}\} = 0$

$$\left\{\boldsymbol{\sigma_x}, \boldsymbol{\sigma_y}\right\} = \boldsymbol{\sigma_x}\boldsymbol{\sigma_y} + \boldsymbol{\sigma_y}\boldsymbol{\sigma}$$

$$\{\boldsymbol{\sigma_x}, \boldsymbol{\sigma_y}\} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\{\boldsymbol{\sigma_x}, \boldsymbol{\sigma_y}\} = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} + \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = 0$$

Similarly 2 and 3.

Now we have to show that for Pauli spin matrices.

1. $\boldsymbol{\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = I}$
2. $\boldsymbol{\sigma^2 = 3I}$

Now $\boldsymbol{\sigma_x^2} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \mathrm{I}$

Similarly $\boldsymbol{\sigma_y^2 = \sigma_z^2 = I}$

Now $\boldsymbol{\sigma^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = I + I + I = 3I}$

Now We have to show that For Pauli spin matrices

1. $\boldsymbol{[\sigma_z, \sigma_+] = 2\sigma_+}$
2. $\boldsymbol{[\sigma_z, \sigma_-] = 2\sigma_-}$

Now $\boldsymbol{[\sigma_z, \sigma_+] = \sigma_z\sigma_+ - \sigma_+\sigma_z}$

$$\boldsymbol{[\sigma_z, \sigma_+] = \sigma_z(\sigma_x + i\sigma_y) - (\sigma_x - i\sigma_y)\sigma_z}$$

$$\boldsymbol{[\sigma_z, \sigma_+] = \sigma_z\sigma_x + i\sigma_z\sigma_y - \sigma_x\sigma_z - i\sigma_y\sigma_z}$$

$$\boldsymbol{[\sigma_z, \sigma_+] = [\sigma_z, \sigma_x] + i[\sigma_z, \sigma_y]}$$

$$\boldsymbol{[\sigma_z, \sigma_+] = 2i\sigma_y + i(-2i\sigma_x)}$$

$$\boldsymbol{[\sigma_z, \sigma_+] = 2(\sigma_x + i\sigma_y) = 2\sigma_+}$$

Similarly part 2.

Eigen value and Eigen vectors of Pauli Spin matrices

As Pauli spin Matrices are

$$\boldsymbol{\sigma_x} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \boldsymbol{\sigma_y} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \boldsymbol{\sigma_z} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

First we take

$$\boldsymbol{\sigma_z = A} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Eigen value equation is

$$\boldsymbol{\det(A - \lambda I) = 0}$$

$$\left|\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \lambda\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right| = \mathbf{0}$$

$$\left|\begin{pmatrix} 1-\lambda & 0 \\ 0 & -1-\lambda \end{pmatrix}\right| = \mathbf{0}$$

$$(1-\lambda)(-1-\lambda) - 0 = 0$$

$$-1 - \lambda + \lambda + \lambda^2 = 0$$

$$\lambda^2 = 1 \Rightarrow \lambda = 1, -1$$

When $\lambda = 1$ we have

$$\mathbf{A} - \boldsymbol{\lambda}\mathbf{I} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - 1\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & -2 \end{pmatrix} \widetilde{R} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} by\ \frac{-1}{2} R_2$$

This means that $x_2 = 0$

$$\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} x_1 \\ 0 \end{pmatrix} = x_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

So eigen vector corresponding to $\lambda = 1$

$$/\psi_1 >= \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

Now when $\lambda = -1$ we have

$$\mathbf{A} - \boldsymbol{\lambda}\mathbf{I} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + 1\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix} \widetilde{R} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} by\ \frac{-1}{2} R_2$$

This means that $x_1 = 0$

$$\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} 0 \\ x_2 \end{pmatrix} = x_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

So Eigen vector corresponding to $\lambda = -1$

$$/\psi_2 >= \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Modal matrix will be

$$S = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

By diagonalization

$$S^{-1}AS = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

This is the diagonal matrix which contains eigen values at diagonal.

Similarly Eigen values of $\boldsymbol{\sigma_x}$ **and** $\boldsymbol{\sigma_y}$ **are** $\lambda = -1, 1$.

Eigen vectors of $\boldsymbol{\sigma_x}$ **are** $/\psi_1 >= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $/\psi_2 >= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

Eigen vectors of $\boldsymbol{\sigma_y}$ **are** $/\psi_1 >= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}$ and $/\psi_2 >= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}$

Solved Problems

1. Prove that
   $[L_i, L_j] = i\hbar\mathcal{E}_{ijk}L_k$ Where $i, j, k = x, y, z$ and $\mathcal{E}_{ijk}$ is Levi-Civita tensor.

$$\mathcal{E}_{ijk} = \begin{cases} 1 & For\ even\ permutations\ of\ i,j,k \\ -1 & For\ odd\ permutations\ of\ i,j,k \\ 0 & If\ two\ or\ more\ indices\ are\ equel \end{cases}$$

Solution

If $i = x$ and $j = y$ i.e even permutation then $\mathcal{E}_{ijk} = 1$ So,

$$\left[L_x, L_y\right] = i\hbar L_z$$

If $i = y$ and $j = x$ i.e odd permutation then $\mathcal{E}_{ijk} = -1$ So,

$$\left[L_y, L_x\right] = -i\hbar L_z$$

If $i = x$ and $j = x$ i.e two indices are same then $\mathcal{E}_{ijk} = 0$ So,

$$[L_x, L_x] = 0$$

2. Prove that
   $\left[L_i, P_j\right] = i\hbar\mathcal{E}_{ijk}P_k$ Where $i,j,k = x,y,z$ and $\mathcal{E}_{ijk}$ is Levi-Civita tensor.

$$\mathcal{E}_{ijk} = \begin{cases} 1 & For\ even\ permutations\ of\ i,j,k \\ -1 & For\ odd\ permutations\ of\ i,j,k \\ 0 & If\ two\ or\ more\ indices\ are\ equel \end{cases}$$

Solution

If $i = x$ and $j = y$ i.e even permutation then $\mathcal{E}_{ijk} = 1$ So,

$$\left[L_x, P_y\right] = i\hbar P_z$$

If $i = y$ and $j = x$ i.e odd permutation then $\mathcal{E}_{ijk} = -1$ So,

$$\left[L_y, P_x\right] = -i\hbar P_z$$

If $i = x$ and $j = x$ i.e two indices are same then $\mathcal{E}_{ijk} = 0$ So,

$$[L_x, P_x] = 0$$

3. Prove that
   $\left[L_i, x_j\right] = i\hbar\mathcal{E}_{ijk}x_k$ Where $i,j,k = x,y,z$ and $\mathcal{E}_{ijk}$ is Levi-Civita tensor.

$$\mathcal{E}_{ijk} = \begin{cases} 1 & For\ even\ permutations\ of\ i,j,k \\ -1 & For\ odd\ permutations\ of\ i,j,k \\ 0 & If\ two\ or\ more\ indices\ are\ equel \end{cases}$$

Solution

If $i = x$ and $j = y$ i.e even permutation then $\mathcal{E}_{ijk} = 1$ So,

$$[L_x, y] = i\hbar z$$

If $i = y$ and $j = x$ i.e odd permutation then $\mathcal{E}_{ijk} = -1$ So,

$$[L_y, x] = -i\hbar z$$

If $i = x$ and $j = x$ i.e two indices are same then $\mathcal{E}_{ijk} = 0$ So,

$$[L_x, x] = 0$$

4. Given that in spherical polar coordinates $L_z = -i\hbar\frac{\partial}{\partial\Phi}$, show that
   a. $[L_z, cos\Phi] = i\hbar sin\Phi$
   b. $[L_z, sin\Phi] = -i\hbar cos\Phi$
   c. $[L_z, sin2\Phi] = -2i\hbar cos2\Phi$

   Solution
   a. $[L_z, cos\Phi] = i\hbar sin\Phi$

$$[L_z, cos\Phi]\psi = L_z cos\Phi\psi - cos\Phi L_z L_z$$

$$[L_z, cos\Phi]\psi = -i\hbar\frac{\partial}{\partial\Phi}(cos\Phi\psi) + i\hbar cos\Phi\frac{\partial}{\partial\Phi}L_z$$

$$[L_z, cos\Phi]\psi = +i\hbar\psi sin\Phi - i\hbar cos\Phi\frac{\partial\psi}{\partial\Phi} + i\hbar cos\Phi\frac{\partial\psi}{\partial\Phi}$$

$$\Rightarrow [L_z, cos\Phi] = i\hbar sin\Phi$$

Similarly Part b and c.

5. Prove that whether or not the Z-component of angular momentum and azimothal angle can be measured precisely and at a same time?
   Solution
   We know that

$$[L_z, \Phi]\psi = L_z\Phi\psi - \Phi L_z\psi$$

$$[L_z, \Phi]\psi = -i\hbar\frac{\partial}{\partial\Phi}\Phi\psi + i\hbar\Phi\frac{\partial}{\partial\Phi}\psi$$

$$[L_z, \Phi]\psi = -i\hbar\psi - i\hbar\Phi\frac{\partial\psi}{\partial\Phi} + i\hbar\Phi\frac{\partial\psi}{\partial\Phi}$$

$$[L_z, \Phi] = -i\hbar$$

   This result shows that $L_z\ and\ \Phi$ do not commute so, these cannot be measured precisely at a same time.
6. Determine whether or not the wave function $\sin m\Phi$ is eigen function of L_z?
   Solution
   Now we operate L_z on $\sin m\Phi$

$$L_z \sin m\Phi = -i\hbar \frac{\partial}{\partial \Phi} \sin m\Phi = -i\hbar m \cos m\Phi$$

By definition of Eigen function

$$\hat{A}\psi = c\psi$$

So, $\sin m\Phi$ is not an Eigen function of L_z.

7. Show that $Y_l^{m^*}(\theta, \emptyset) = (-1)^m \, Y_l^{-m}(\theta, \emptyset)$

Solution

From definition of spherical harmonics

$$Y_l^m(\theta, \emptyset) = (-\mathbf{1})^{\boldsymbol{m}} \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(cos\theta) e^{im\emptyset}$$

$$Y_l^{m^*}(\theta, \emptyset) = (-\mathbf{1})^{\boldsymbol{m}} \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(cos\theta) e^{-im\emptyset}$$

Now

$$P_l^m(cos\theta) = (-\mathbf{1})^{\boldsymbol{m}} \frac{(l+m)!}{(l-m)!} P_l^{-m}(cos\theta)$$

$$Y_l^{m^*}(\theta, \emptyset) = (-\mathbf{1})^{\boldsymbol{m}} \left((-\mathbf{1})^{\boldsymbol{m}} \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} \frac{(l+m)!}{(l-m)!} P_l^{-m}(cos\theta) e^{-im\emptyset} \right)$$

$$\Rightarrow \; Y_l^{m^*}(\theta, \emptyset) = (-\mathbf{1})^{\boldsymbol{m}} \, Y_l^{-m}(\theta, \emptyset)$$

8. Can all the components of total angular momentum determine at a same time?

Solution

We know that

$[J_x, J_y] = i\hbar J_z \quad , \quad [J_y, J_z] = i\hbar J_x$ and $[J_z, J_x] = i\hbar J_y$

By uncertainty relation

$$\Delta\hat{A}\Delta\hat{B} \geq \left| \langle \frac{[\hat{A}, \hat{B}]}{2i} \rangle \right|$$

If $\Delta\hat{A}\Delta\hat{B} = 0$, then values can be determined simultaneously, otherwise not.

For $[J_x, J_y] = i\hbar J_z$

$$\Delta J_x \Delta J_y \geq \left| \langle \frac{[J_x, J_y]}{2i} \rangle \right|$$

$$\Delta J_x \Delta J_y \geq \left| \langle \frac{i\hbar J_z}{2i} \rangle \right|$$

$$\Delta J_x \Delta J_y \geq \frac{\hbar}{2}\langle J_z \rangle$$

Similarly

$$\Delta J_y \Delta J_z \geq \frac{\hbar}{2}\langle J_x \rangle$$

$$\Delta J_z \Delta J_x \geq \frac{\hbar}{2}\langle J_y \rangle$$

These results illustrate that components of total angular momentum cannot determine simultaneously.

9. Show that $[J_x, J_{\mp}] = \mp\hbar J_{\mp}$
10.

CHAPTER 6

IDENTICAL PARTICLES

Identical particles also called **indistinguishable** or **indiscernible particles** are particles that cannot be distinguished from one another, even in principle. Species of identical particles include, but are not limited to elementary particles such as electrons, composite subatomic particles such as atomic nuclei, as well as atoms and molecules. Quasi particles also behave in this way. Although all known indistinguishable particles are "tiny", there is no exhaustive list of all possible sorts of particles nor a clear-cut limit of applicability; see particle statistics #Quantum statistics for detailed explication. There are two main categories of identical particles: bosons, which can share quantum states, and fermions, which do not share quantum states due to the Pauli exclusion principle. Examples of bosons are photons, gluons, phonons, helium-4 nuclei and all mesons. Examples of fermions are electrons, neutrinos, quarks, protons, neutrons, and helium-3 nuclei.

Let we have two identical particles 1 and 2, located at state a and b with position vectors from a point $\mathbf{r_1}$ and $\mathbf{r_2}$ respectively. Now the wave function of these particles is written as

$$\psi_{1,2}(r_1, r_2) = C_{12}\psi_a(r_1)\psi_b(r_2) + C_{21}\psi_a(r_2)\psi_b(r_1)$$

$$/\psi_{1,2}(r_1, r_2) >= C_{12}/\psi_a(r_1) >/\psi_b(r_2) > + C_{21}/\psi_a(r_2) >/\psi_b(r_1) >$$

$$/\psi_{1,2} >= C_{12}/1, a >/2, b > + C_{21}/1, b >/2, a >$$

Now when we interchange their positions that is $r_1 \rightleftharpoons r_2$ then

$$\left|/\psi_{1,2} >\right|^2 = \left|/\psi_{2,1} >\right|^2$$

$$/\psi_{1,2} >= A/\psi_{2,1} >$$

So we can write

$$C_{12}/1, a >/2, b > + C_{21}/1, b >/2, a >= A(C_{21}/1, a >/2, b > + C_{12}/1, b >/2, a >)$$

Comparing both sides

$$C_{12} = AC_{21} \text{ ----------(1)}$$

$$C_{21} = AC_{12} \text{ ----------(2)}$$

Put value of C_{21} in equation 1

$$C_{12} = A^2 C_{12} \Rightarrow A^2 = 1 \Rightarrow A = \pm 1$$

So equation 2 becomes

$$C_{21} = \pm C_{12}$$

Hence

$$/\psi_{1,2} >= C_{12}/1, a >/2, b > \pm C_{12}/1, b >/2, a >$$

$$/\psi_{1,2} >= C_{12}[/1, a >/2, b > \pm/1, b >/2, a >]$$

Or $$\psi_{1,2}(r_1, r_2) = C_{12}[\psi_a(r_1)\psi_b(r_2) \pm \psi_a(r_2)\psi_b(r_1)]$$

For two identical bosons

$$\psi_{1,2}(r_1, r_2) = C_{12}[\psi_a(r_1)\psi_b(r_2) + \psi_a(r_2)\psi_b(r_1)]$$

For two identical femions

$$\psi_{1,2}(r_1, r_2) = C_{12}[\psi_a(r_1)\psi_b(r_2) - \psi_a(r_2)\psi_b(r_1)]$$

Here C_{12} is constant, if we normalized above wave functions $C_{12} = \frac{1}{\sqrt{2}}$

So we can write normalized wave function as

$$\psi_{1,2}(r_1, r_2) = \frac{1}{\sqrt{2}}[\psi_a(r_1)\psi_b(r_2) \pm \psi_a(r_2)\psi_b(r_1)]$$

Pauli,s Exclusion principle: According to Pauli no two fermions can occupy same state.

As for Fermions

$$\psi_{1,2}(r_1, r_2) = \frac{1}{\sqrt{2}}[\psi_a(r_1)\psi_b(r_2) - \psi_a(r_2)\psi_b(r_1)]$$

If a=b and r_1=r_2 then

$$\psi_{1,2}(r_1, r_2) = \frac{1}{\sqrt{2}}[\psi_a(r_1)\psi_a(r_1) - \psi_a(r_1)\psi_a(r_1)] = 0$$

Wave function vanish.So no two fermions can have same state and position simultaneously. This is Pauli's Exclusion principle.

For Bosons if a=b and r_1=r_2 then

$$\psi_{1,2}(r_1, r_2) = \frac{1}{\sqrt{2}}[\psi_a(r_1)\psi_b(r_2) + \psi_a(r_2)\psi_b(r_1)]$$

$$\psi_{1,2}(r_1, r_2) = \frac{1}{\sqrt{2}}[\psi_a(r_1)\psi_a(r_1) + \psi_a(r_1)\psi_a(r_1)]$$

$$\psi_{1,2}(r_1, r_2) = \frac{2}{\sqrt{2}}[\psi_a(r_1)\psi_a(r_1)] \neq 0$$

So for bosons wave function does not vanish. So, bosons do not obey Pauli's exclusion Principle.

Hamiltonian Of two identical Fermions

Hamiltonian of two fermions is written as

$$H = \frac{{P_1}^2}{2m_1} + \frac{{P_2}^2}{2m_2} + V_{12}$$

$$H = \frac{-\hbar^2}{2m}\left({\nabla_1}^2 + {\nabla_2}^2\right) + \frac{e^2}{4\pi\epsilon_o(r_2 - r_1)}$$

Now we find energy eigen value

$$\langle E\rangle = \langle\psi_{1,2}|H|\psi_{1,2}\rangle$$

As $$/\psi_{1,2} >= \frac{1}{\sqrt{2}}[/1, a >/2, b > -/1, b >/2, a >]$$

$$\langle E\rangle = \frac{1}{2}[\langle 1, a|\langle 2, b|H|1, a\rangle|2, b\rangle + \langle 2, a|\langle 1, b|H|2, a\rangle|1, b\rangle - \langle 1, a|\langle 2, b|H|2, a\rangle|1, b\rangle - \langle 2, a|\langle 2, b|H|2, a\rangle|2, b\rangle]$$

$$\langle E\rangle = \frac{1}{2}[2\langle 1, a|\langle 2, b|H|1, a\rangle|2, b\rangle]$$

$$\langle E\rangle = \left[\left\langle 1, a\middle|\left\langle 2, b\middle|\frac{-\hbar^2{\nabla_1}^2}{2m}\middle|1, a\right\rangle\middle|2, b\right\rangle + \left\langle 1, a\middle|\left\langle 2, b\middle|\frac{-\hbar^2{\nabla_2}^2}{2m}\middle|1, a\right\rangle\middle|2, b\right\rangle + \left\langle 1, a\middle|\left\langle 2, b\middle|\frac{e^2}{4\pi\epsilon_o(r_2 - r_1)}\middle|1, a\right\rangle\middle|2, b\right\rangle\right]$$

$$\langle E\rangle = \langle E_1\rangle + \langle E_2\rangle + \langle P.E_{12}\rangle$$

N number of identical particles

1. **Non Interacting identical particles**: Let we have N number of non interacting identical particles with M modes to fit then wave function is written as
   $$/\psi >= /1, a >/2, b >/3, c > - - -/N, n >$$
   That is we can fit N particles in n modes. This scheme is not valid for Bosons and fermions.
2. N Bosons: The wave function of N number of bosons can be written as
   $$/\psi_{Boson} >= \sum_P P\,/1, a >/2, b >/3, c > - - -/N, n >$$
   Her P is the permutation operator. The above wave function remains unchanged if we permute the position of two particles.
3. N Fermions: The wave function of N number of fermions is written as
   $$/\psi_{Fermion} >= \frac{1}{N!}\sum_{P=1}^{N!} \pm P\,/1, a >/2, b >/3, c > - - -/N, n >$$

Her + sign is for even Permutation and – sign is for odd permutation. Permutation will depend on unique pair wise distribution of two particles.

Other method of fermions wave function is Slater determinant.

$$/\psi_{Fermion}>=\frac{1}{N!}\begin{vmatrix} /1,a> & /2,a> & /3,a>\cdots & /n,a> \\ /1,b> & /2,b> & /3,b>\cdots & /n,b> \\ \vdots & \vdots & \vdots \quad \vdots & \vdots \end{vmatrix}$$

In this determinant if two particles are in same state, two columns will be same so determinant will be zero.If two states will be same then two rows will be same.Again determinant will be zero. Similarly if two columns are interchanged the sign of determinant will also change, this will represent the two particles exchange position.

Particles Statistics

1. Non ineracting particles:If we have N numbers of non ineraction identical particles Have M modes to fit than first particle has M modes to fit,Second particle has M modes to fit and so on Nth particles has M modes to fit .So Multipilicity can be wriiten as

$$Multiplicity = Probebility\ = N_{basis} = M^N$$

2. Bosons: Let we have N bosons with M modes to fit then we can imagine M states as M bins.First particle has M bins to fit. When particle put in the bin the scond particle has two ways to fit in the bin ,befor or after the first particle.That is first particle divide the bin into two compartments.So first paricle allow the same bin or remaing M-1 bins to second particle.So there are M+1 ways to fit the second paricle.In the same fashon third particle has M+2 ways to fit in the bins and So on. So possible ways for N bosons will be

M(M+1)(M+2)------(M+N-1)

So Multipilicity can be written as

$$Multiplicity = Probebility\ = N_{basis} = \frac{(M+N-1)!}{N!\,(M-1)!}$$

Fermions: Let we have N fermions and M states.First fermion has M choices to Fit.Second fermion hasb M-1 choices and so on .Repetition is not allowed. So Multipilicity can be written as

$$Multiplicity = Probebility\ = N_{basis} = \frac{M!}{N!\,(M-N)!}$$

CHAPTER 7
THREE DIMENSIONAL SYSTEMS

Schrodinger's equation for Hydrogen atom

Hydrogen is the simplest of all the atoms one proton and one electron. Electron is revolving around the nucleus in an orbit. The kinetic energy of electron is

$$T = \frac{p^2}{2m} \text{ ------- (1)}$$

And potential energy is

$$V = \frac{-Ze^2}{r} \text{ -------- (2)}$$

Hamiltonian operator will be

$$H = T + V$$

$$H = \frac{p^2}{2m} + \frac{-Ze^2}{r}$$

As $p^2 = -\hbar^2\nabla^2$ so

$$H = \frac{-\hbar^2\nabla^2}{2m} + \frac{-Ze^2}{r} \text{ ------- (3)}$$

For hydrogen Z=1

Now the Schrodinger's equation in Cartesian coordinates is

$$\nabla^2\psi(\mathrm{r}) + \frac{2m}{\hbar^2}(E - V)\psi(\mathrm{r}) = 0 \text{ ------- (4)}$$

Since potential energy of the electron is spherically symmetric so we cannot solve this equation by using Cartesian coordinates. We express the Schrodinger's equation in term of spherical coordinates(r, θ, ϕ).

Now ∇^2 in spherical polar coordinates is

$$\nabla^2 = \frac{1}{r^2}\frac{\eth}{\eth r}\left(r^2\frac{\eth}{\eth r}\right) + \frac{1}{r^2\sin\theta}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth}{\eth\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\eth^2}{\eth\phi^2}$$

And $$\psi(\mathrm{r}) = \psi = \psi(\mathrm{r}, \theta, \phi)$$

Now Schrodinger's equation 3 will become

$$\frac{1}{r^2}\frac{\eth}{\eth r}\left(r^2\frac{\eth\psi}{\eth r}\right) + \frac{1}{r^2\sin\theta}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\psi}{\eth\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\eth^2\psi}{\eth\phi^2} + \frac{2m}{\hbar^2}(E - \frac{-Ze^2}{r})\psi = 0$$

$\frac{1}{r^2}\frac{\eth}{\eth r}\left(r^2\frac{\eth\psi}{\eth r}\right) + \frac{1}{r^2\sin\theta}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\psi}{\eth\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\eth^2\psi}{\eth\phi^2} + \frac{2m}{\hbar^2}(E + \frac{e^2}{r})\psi = 0$ ------- (5)

We solve equation 5 by variable separation method such that

$$\psi(\mathrm{r}, \theta, \phi) = \mathbf{R}(r)\boldsymbol{\theta}(\theta)\boldsymbol{\Phi}(\Phi) = \mathbf{R}\boldsymbol{\theta}\boldsymbol{\Phi}$$

So above equation will be

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{R\theta\Phi}}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial \mathbf{R\theta\Phi}}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\mathbf{R\theta\Phi}}{\partial\phi^2}+\frac{2m}{\hbar^2}(E+\frac{e^2}{r})\mathbf{R\theta\Phi}=0$$

$$\frac{\boldsymbol{\theta\Phi}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{R}}{\partial r}\right)+\frac{\mathbf{R\Phi}}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial \boldsymbol{\theta}}{\partial\theta}\right)+\frac{\mathbf{R}\boldsymbol{\theta}}{r^2\sin^2\theta}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}+\frac{2m}{\hbar^2}(E+\frac{e^2}{r})\mathbf{R\theta\Phi}=0$$

Divide by $\mathbf{R\theta\Phi}$

$$\frac{\boldsymbol{\theta\Phi}}{\mathbf{R\theta\Phi}r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{R}}{\partial r}\right)+\frac{\mathbf{R\Phi}}{\mathbf{R\theta\Phi}r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial \boldsymbol{\theta}}{\partial\theta}\right)+\frac{\mathbf{R}\boldsymbol{\theta}}{\mathbf{R\theta\Phi}r^2\sin^2\theta}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}+\frac{2m}{\hbar^2}(E+\frac{e^2}{r})\frac{\mathbf{R\theta\Phi}}{\mathbf{R\theta\Phi}}=0$$

$$\frac{\mathbf{1}}{\mathbf{R}r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{R}}{\partial r}\right)+\frac{\mathbf{1}}{\boldsymbol{\theta}r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial \boldsymbol{\theta}}{\partial\theta}\right)+\frac{\mathbf{1}}{\boldsymbol{\Phi}r^2\sin^2\theta}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}+\frac{2m}{\hbar^2}(E+\frac{e^2}{r})=0$$

$$\frac{\mathbf{1}}{\mathbf{R}r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{R}}{\partial r}\right)+\frac{2m}{\hbar^2}\left(E+\frac{e^2}{r}\right)=-\frac{\mathbf{1}}{\boldsymbol{\theta}r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial \boldsymbol{\theta}}{\partial\theta}\right)-\frac{\mathbf{1}}{\boldsymbol{\Phi}r^2\sin^2\theta}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}$$

Multiply by r^2

$$\frac{1}{\mathbf{R}}\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{R}}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(E+\frac{e^2}{r}\right)=-\frac{\mathbf{1}}{\boldsymbol{\theta}\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial \boldsymbol{\theta}}{\partial\theta}\right)-\frac{\mathbf{1}}{\boldsymbol{\Phi}\sin^2\theta}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}$$

In this above equation right side is a function of $\boldsymbol{\theta}$ and $\boldsymbol{\Phi}$ while left side is the function of $\mathbf{R}$.So bothare equal to some constant sayλ. Here $\lambda = l(l+1)$

$$\frac{1}{\mathbf{R}}\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{R}}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(E+\frac{e^2}{r}\right)=-\frac{\mathbf{1}}{\boldsymbol{\theta}\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial \boldsymbol{\theta}}{\partial\theta}\right)-\frac{\mathbf{1}}{\boldsymbol{\Phi}\sin^2\theta}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}=l(l+1)$$

$$\frac{1}{\mathbf{R}}\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{R}}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(E+\frac{e^2}{r}\right)=l(l+1)\text{ ------- (A)}$$

This equation is called radial equation. Similarly

$$-\frac{\mathbf{1}}{\boldsymbol{\theta}\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial \boldsymbol{\theta}}{\partial\theta}\right)-\frac{\mathbf{1}}{\boldsymbol{\Phi}\sin^2\theta}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}=l(l+1)$$

$$\frac{\mathbf{1}}{\boldsymbol{\theta}\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial \boldsymbol{\theta}}{\partial\theta}\right)+\frac{\mathbf{1}}{\boldsymbol{\Phi}\sin^2\theta}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}=-l(l+1)\text{------- (B)}$$

This equation is called angular equation. We solve this equation

$$\frac{\mathbf{1}}{\boldsymbol{\theta}\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial \boldsymbol{\theta}}{\partial\theta}\right)+l(l+1)=\frac{-\mathbf{1}}{\boldsymbol{\Phi}\sin^2\theta}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}$$

$$\frac{\sin\theta}{\boldsymbol{\theta}}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right)+l(l+1)\sin^2\theta=\frac{-\mathbf{1}}{\boldsymbol{\Phi}}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}$$

In this equation right side is the function of $\boldsymbol{\Phi}$and left side is the function of$\boldsymbol{\theta}$**.** So both areequal to some constantm^2.

$$\frac{\sin\theta}{\boldsymbol{\theta}}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right)+l(l+1)=\frac{-\mathbf{1}}{\boldsymbol{\Phi}}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}=\mathrm{m}^2$$

That is

$$\frac{\sin\theta}{\boldsymbol{\theta}}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right)+l(l+1)=\mathrm{m}^2 \text{ -------(C)}$$

And

$$\frac{\mathbf{1}}{\boldsymbol{\Phi}}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}=-\mathrm{m}^2 \text{ ------- (D)}$$

Equation C and D are the equation of $\boldsymbol{\theta}$and$\boldsymbol{\Phi}$respectively.

Solution of$\boldsymbol{\Phi}$ equation D

$$\text{As}\frac{\mathbf{1}}{\boldsymbol{\Phi}}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}=-\mathrm{m}^2$$

$$\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}=-\mathrm{m}^2\boldsymbol{\Phi}$$

$$\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}+\mathrm{m}^2\boldsymbol{\Phi}=0$$

This is second order differential equation whose solution is

$$\boldsymbol{\Phi}=\Phi_o e^{im\phi}$$

Here $\mathrm{m}=0,\pm1,\pm2,---$ and Φ_o is constant.

The normalized wave function will be

$$\boldsymbol{\Phi}=\frac{1}{\sqrt{2\pi}}e^{im\phi}$$

Solution of$\boldsymbol{\theta}$ equation C

As θ equation is

$$\frac{\sin\theta}{\boldsymbol{\theta}}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right)+l(l+1)\sin^2\theta=\mathrm{m}^2$$

$$\frac{1}{\sin\boldsymbol{\theta}}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right)+l(l+1)\boldsymbol{\theta}=\frac{\mathrm{m}^2\boldsymbol{\theta}}{\sin^2\theta}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right)+\left\{l(l+1)-\frac{\mathrm{m}^2}{\sin^2\theta}\right\}\boldsymbol{\theta}=0$$

This is special type of differential equation. We solve it by substitution method.

Let $x=\cos\theta$

$$\frac{\partial}{\partial\theta}=\frac{\partial}{\partial x}\frac{\partial x}{\partial\theta}=-\sin\theta\frac{\partial}{\partial x}$$

So above equation will become

$$\frac{1}{\sin\theta}\left(-\sin\theta\frac{\partial}{\partial x}\right)\left(\sin\theta\left(-\sin\theta\frac{\partial}{\partial x}\right)\boldsymbol{\theta}\right)+\left\{l(l+1)-\frac{\mathrm{m}^2}{1-\cos^2\theta}\right\}\boldsymbol{\theta}=0$$

$$\frac{\partial}{\partial x}\left(\sin^2\theta\frac{\partial\boldsymbol{\theta}}{\partial x}\right)+\left\{l(l+1)-\frac{\mathrm{m}^2}{1-\cos^2\theta}\right\}\boldsymbol{\theta}=0$$

$$\frac{\partial}{\partial x}\left((1-\cos^2\theta)\frac{\partial\boldsymbol{\theta}}{\partial x}\right)+\left\{l(l+1)-\frac{\mathrm{m}^2}{1-\cos^2\theta}\right\}\boldsymbol{\theta}=0$$

$$\frac{\partial}{\partial x}\left((1-x^2)\frac{\partial\boldsymbol{\theta}}{\partial x}\right)+\left\{l(l+1)-\frac{\mathrm{m}^2}{1-x^2}\right\}\boldsymbol{\theta}=0$$

$$(1-x^2)\frac{\partial^2\boldsymbol{\theta}}{\partial x^2}-2x\frac{\partial\boldsymbol{\theta}}{\partial x}+\left\{l(l+1)-\frac{\mathrm{m}^2}{1-x^2}\right\}\boldsymbol{\theta}=0$$

This is associated Legendre's polynomial equation whose solution is

$$P_l^m=\frac{(1-x^2)^{\frac{m}{2}}}{2^l l!}\frac{\partial^{m+l}}{\partial x^{m+l}}(x^2-1)^l$$

Some associated Legendre polynomials are

$$P_0^0(x)=1\ \ or\quad P_0^0(cos\theta)=1$$

$$P_1^1(x)=(1-x^2)^{\frac{1}{2}}\ \ or\quad P_1^1(cos\theta)=sin\theta$$

$$P_2^1(x)=3x(1-x^2)^{\frac{1}{2}}\ \ or\quad P_2^1(cos\theta)=3cos\theta sin\theta$$

$$P_2^2(x) = 3(1-x^2)\ or \quad P_2^2(cos\theta) = 3sin^2\theta$$

$$P_3^1(x) = \frac{3}{2}(5x^2-1)(1-x^2)^{\frac{1}{2}}\ or \quad P_3^1(cos\theta) = \frac{3}{2}(5cos^2\theta - 1)sin\theta$$

$$P_3^2(x) = 15x(1-x^2)\ or \quad P_3^2(cos\theta) = 15cos\theta sin^2\theta$$

$$P_3^3(x) = 15x(1-x^2)^{\frac{3}{2}}\ or \quad P_3^3(cos\theta) = 15sin^3\theta$$

Now the solution of $\boldsymbol{\theta}$ equation will be

$$\boldsymbol{\theta_{lm}} = \sqrt{\frac{(2l+1)(l-m)!}{2\pi(l+m)!}}P_l^m(cos\theta)$$

Solution of$R$ equation A

As radial equation A is

$$\frac{1}{\mathbf{R}}\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{R}}{\partial r}\right) + \frac{2mr^2}{\hbar^2}\left(E + \frac{e^2}{r}\right) = l(l+1)$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{R}}{\eth r}\right) + \left\{\frac{2mr^2}{\hbar^2}\left(E + \frac{e^2}{r}\right) - l(l+1)\right\}\mathbf{R} = 0$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{R}}{\partial r}\right) + \left\{\frac{2m}{\hbar^2}\left(E + \frac{e^2}{r}\right) - \frac{l(l+1)}{r^2}\right\}\mathbf{R} = 0$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{R}}{\partial r}\right) + \left\{\frac{2mE}{\hbar^2} + \frac{2me^2}{\hbar^2 r} - \frac{l(l+1)}{r^2}\right\}\mathbf{R} = 0$$

Put $\rho = \alpha r$ so$r = \frac{\alpha}{\rho}$

$$\frac{\alpha^2}{\rho^2}\frac{\partial}{\partial \rho}\left(\rho^2\frac{\partial \mathbf{R}}{\partial \rho}\right) + \left\{\frac{2mE}{\hbar^2} + \frac{2me^2\alpha}{\hbar^2\rho} - \frac{l(l+1)\alpha^2}{\rho^2}\right\}\mathbf{R} = 0$$

$$\frac{1}{\rho^2}\frac{\partial}{\partial \rho}\left(\rho^2\frac{\partial \mathbf{R}}{\partial \rho}\right) + \left\{\frac{2mE}{\alpha^2\hbar^2} + \frac{2me^2}{\hbar^2\rho\alpha} - \frac{l(l+1)}{\rho^2}\right\}\mathbf{R} = 0$$

For bound state $E < 0$i.e.$E = -E$

$$\frac{1}{\rho^2}\frac{\partial}{\partial \rho}\left(\rho^2\frac{\partial \mathbf{R}}{\partial \rho}\right) + \left\{\frac{-2mE}{\alpha^2\hbar^2} + \frac{2me^2}{\hbar^2\rho\alpha} - \frac{l(l+1)}{\rho^2}\right\}\mathbf{R} = 0$$

Put $\frac{8mE}{\hbar^2} = \alpha^2$ and $\frac{2me^2}{\hbar^2\alpha} = \lambda$

So

$$\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial\mathbf{R}}{\partial\rho}\right)+\left\{\frac{-1}{4}+\frac{\lambda}{\rho}-\frac{l(l+1)}{\rho^2}\right\}\mathbf{R}=0$$

$$\Longrightarrow\frac{\partial^2\mathbf{R}}{\partial\rho^2}+\frac{2}{\rho}\frac{\partial\mathbf{R}}{\partial\rho}+\left\{\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right\}\mathbf{R}=0\text{------- (E)}$$

If $\rho\to\infty$

$$\frac{\eth^2\mathbf{R}}{\eth\rho^2}-\frac{\mathbf{R}}{\mathbf{4}}=0$$

This is second order differential equation whose solution will be

$$\mathbf{R}=Ae^{\frac{\rho}{2}}+Be^{\frac{-\rho}{2}}$$

As $\rho\to\infty$ so first term of the solution vanish only second term is possible solution.

$$\mathbf{R}=Be^{\frac{-\rho}{2}}$$

B is constant such that

$$\mathbf{B}=F(\rho)$$

So

$$\mathbf{R}=F(\rho)e^{\frac{-\rho}{2}}$$

$$\frac{\partial\mathbf{R}}{\partial\rho}=\frac{\partial F}{\partial\rho}e^{\frac{-\rho}{2}}-\frac{1}{2}Fe^{\frac{-\rho}{2}}$$

$$\frac{\partial^2\mathbf{R}}{\partial\rho^2}=\frac{\partial^2F}{\partial\rho^2}e^{\frac{-\rho}{2}}-\frac{1}{2}\frac{\partial F}{\partial\rho}e^{\frac{-\rho}{2}}-\frac{1}{2}\frac{\partial F}{\partial\rho}e^{\frac{-\rho}{2}}+\frac{1}{4}Fe^{\frac{-\rho}{2}}$$

$$\frac{\partial^2\mathbf{R}}{\partial\rho^2}=\frac{\partial^2F}{\partial\rho^2}e^{\frac{-\rho}{2}}-\frac{\partial F}{\partial\rho}e^{\frac{-\rho}{2}}+\frac{1}{4}Fe^{\frac{-\rho}{2}}$$

Put value of $\frac{\partial^2\mathbf{R}}{\partial\rho^2}$, $\frac{\partial\mathbf{R}}{\partial\rho}$ and $\mathbf{R}$in equation E

$$\frac{\partial^2F}{\partial\rho^2}e^{\frac{-\rho}{2}}-\frac{\partial F}{\partial\rho}e^{\frac{-\rho}{2}}+\frac{1}{4}Fe^{\frac{-\rho}{2}}+\frac{2}{\rho}\left(\frac{\partial F}{\partial\rho}e^{\frac{-\rho}{2}}-\frac{1}{2}Fe^{\frac{-\rho}{2}}\right)+\left\{\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right\}Fe^{\frac{-\rho}{2}}=0$$

$$\frac{\partial^2F}{\partial\rho^2}-\frac{\partial F}{\partial\rho}+\frac{1}{4}F+\frac{2}{\rho}\left(\frac{\partial F}{\partial\rho}-\frac{1}{2}F\right)+\left\{\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right\}F=0$$

$$\frac{\partial^2 F}{\partial \rho^2}+\left(\frac{2}{\rho}-1\right)\frac{\partial F}{\partial \rho}-\frac{F}{\rho}+\frac{1}{4}F+\left\{\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right\}F=0$$

$$\frac{\partial^2 F}{\partial \rho^2}+\left(\frac{2}{\rho}-1\right)\frac{\partial F}{\partial \rho}-\frac{F}{\rho}+\frac{1}{4}F-\frac{1}{4}F+\left\{\frac{\lambda}{\rho}-\frac{l(l+1)}{\rho^2}\right\}F=0$$

$\frac{\partial^2 F}{\partial \rho^2}+\left(\frac{2}{\rho}-1\right)\frac{\partial F}{\partial \rho}+\left\{\frac{\lambda-1}{\rho}-\frac{l(l+1)}{\rho^2}\right\}F=0$ ------- (F)

This is second order differential equation. We solve it by power series method. Such that

$$F=\sum_{r=0}^{\infty}\alpha_r\rho^{k+r}$$

$$\frac{\partial F}{\partial \rho}=\sum_{r=0}^{\infty}(k+r)\alpha_r\rho^{k+r-1}$$

$$\frac{\partial^2 F}{\partial \rho^2}=\sum_{r=0}^{\infty}(k+r)(k+r-1)\alpha_r\rho^{k+r-2}$$

So equation F will become

$$\sum_{r=0}^{\infty}(k+r)(k+r-1)\alpha_r\rho^{k+r-2}+\left(\frac{2}{\rho}-1\right)\sum_{r=0}^{\infty}(k+r)\alpha_r\rho^{k+r-1}+\left\{\frac{\lambda-1}{\rho}-\frac{l(l+1)}{\rho^2}\right\}\sum_{r=0}^{\infty}\alpha_r\rho^{k+r}=0$$

$$\rho^2\sum_{r=0}^{\infty}(k+r)(k+r-1)\alpha_r\rho^{k+r-2}+\rho^2\left(\frac{2}{\rho}-1\right)\sum_{r=0}^{\infty}(k+r)\alpha_r\rho^{k+r-1}+\rho^2\left\{\frac{\lambda-1}{\rho}-\frac{l(l+1)}{\rho^2}\right\}\sum_{r=0}^{\infty}\alpha_r\rho^{k+r}=0$$

$$\sum_{r=0}^{\infty}(k+r)(k+r-1)\alpha_r\rho^{k+r}+2\sum_{r=0}^{\infty}(k+r)\alpha_r\rho^{k+r}-\sum_{r=0}^{\infty}(k+r)\alpha_r\rho^{k+r+1}+(\lambda-1)\sum_{r=0}^{\infty}\alpha_r\rho^{k+r+1}-l(l+1)\sum_{r=0}^{\infty}\alpha_r\rho^{k+r}=0$$

$$\sum_{r=0}^{\infty}\{(k+r)(k+r-1)+2(k+r)-l(l+1)\}\alpha_r\rho^{k+r}-\sum_{r=0}^{\infty}\{(k+r)-(\lambda-1)\}\alpha_r\rho^{k+r+1}=0$$

$$\sum_{r=0}^{\infty}\{(k+r)(k+r-1)+2(k+r)-l(l+1)\}\alpha_r\rho^{k+r}=\sum_{r=0}^{\infty}\{(k+r)-(\lambda-1)\}\alpha_r\rho^{k+r+1}$$

Expend left summation by putting $r=r+1$ and Compere the coefficients of ρ^{k+r+1}

$$\sum_{r=0}^{\infty}\{(k+r+1)(k+r+1-1)+2(k+r+1)-l(l+1)\}\alpha_{r+1}\rho^{k+r+1}=\sum_{r=0}^{\infty}\{(k+r)-(\lambda-1)\}\alpha_r\rho^{k+r+1}$$

$$\{(k+r+1)(k+r)+2(k+r+1)-l(l+1)\}\alpha_{r+1}=(k+r)-(\lambda-1)\}\alpha_r$$

$$\alpha_{r+1} = \frac{\{(k+r)-(\lambda-1)\}}{\{(k+r+1)(k+r)+2(k+r+1)-l(l+1)\}}\alpha_r$$

$$\alpha_{r+1} = \frac{k+r-\lambda+1}{(k+r+1)(k+r+2)-l(l+1)\}}\alpha_r$$

The series will terminate if $\alpha_{r+1} = 0$ so

$$k+r-\lambda+1=0$$

$$\lambda = k+r+1$$

$k+r+1 = imtegers = n$So$\lambda = n$

But $\lambda = \frac{2me^2}{\hbar^2\alpha}$ and $\frac{8mE}{\hbar^2} = \alpha^2$

$$n = \frac{2me^2}{\hbar^2}\frac{\hbar}{\sqrt{8mE}}$$

$$\sqrt{8mE} = \frac{2me^2}{n\hbar}$$

$$8mE = \frac{4m^2e^4}{n^2\hbar^2}$$

$$E = \frac{me^4}{2n^2\hbar^2}$$

For bound energy put $E = -E_n$ so

$$E_n = -\frac{me^4}{2n^2\hbar^2}$$

His is the energy Eigen value of hydrogen atom as obtained by Bohar and well fit with experimental value.

Radial Wave function

As

$$F = \sum_{r=0}^{\infty} \alpha_r \rho^{k+r}$$

We write it as

$$F = \rho^k L(\rho)$$

Here $L(\rho) = \sum_{r=0}^{\infty} \alpha_r \rho^r$ is called Laguerre polynomial. Use value of ***F*** in equation F.

$$\frac{\partial^2 \rho^k L(\rho)}{\partial \rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{\partial \rho^k L(\rho)}{\partial \rho} + \left\{\frac{\lambda - 1}{\rho} - \frac{l(l+1)}{\rho^2}\right\}\rho^k L(\rho) = 0$$

$$\rho^2 L'' + +(2k + 2 - \rho)\rho L' + \{\rho(\lambda - k - 1) + k(k+1) - l(l+1)\}L = 0$$

Put $k = l \; and \; \lambda = n$

$$\rho^2 L'' + +(2l + 2 - \rho)\rho L' + \{\rho(n - l - 1) + l(l+1) - l(l+1)\}L = 0$$

$\rho L^{''} + +(2l + 2 - \rho)L^{'} + (n - l - 1)L = 0$ ------- (G)

This equation is just like associated Laguerre equation of the form

$\rho L^{''p}_{\ q} + +(\boldsymbol{p} + 1 - \rho)L^{'p}_{\ q} + (\boldsymbol{q} - \boldsymbol{p})L^{p}_{q} = 0$ ------- (H)

The solution of equation H isL^{p}_{q}.

Compere equation G and H

$\boldsymbol{p} = 2l + 1 \text{and} \boldsymbol{q} = n + l$

So solution of the equation G will beL^{2l+1}_{n+1}.

Now the radial wave function will be

$$\mathbf{R} = F(\rho)e^{\frac{-\rho}{2}}$$

$$\mathbf{R} = \rho^k L(\rho)e^{\frac{-\rho}{2}}$$

$$\mathbf{R} = \rho^k L^{2l+1}_{n+1} e^{\frac{-\rho}{2}}$$

The normalized wave function will be

$$\mathbf{R_{nl}} = N\rho^l L^{2l+1}_{n+1} e^{\frac{-\rho}{2}}$$

Value of N can be found by the normalized condition of associated Laguerre polynomials.

$$N = \sqrt{\left(\frac{2}{\pi a_o}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}$$

Here$a_o = \frac{\hbar^2}{me^2}$ and $\rho = \frac{2r}{na_o}$ so

$$\mathbf{R_{nl}} = \sqrt{\left(\frac{2}{\pi a_o}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} \rho^l L_{n+1}^{2l+1} e^{\frac{-\rho}{2}}$$

Complete wave function of hydrogen atom

As complete wave function is

$$\psi(\mathrm{r},\theta,\phi) = \mathbf{R}(r)\boldsymbol{\theta}(\theta)\boldsymbol{\Phi}(\Phi) = \mathbf{R_{nl}}\boldsymbol{\theta_{lm}}\boldsymbol{\Phi}$$

$$\psi(\mathrm{r},\theta,\phi) = \mathbf{R_{nl}}\boldsymbol{\theta_{lm}}\boldsymbol{\Phi_m} = \sqrt{\left(\frac{2}{\pi a_o}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} \rho^l L_{n+1}^{2l+1} e^{\frac{-\rho}{2}} \sqrt{\frac{(2l+1)(l-m)!}{2\pi(lm)!}} P_l^m(cos\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

Quantum numbers

In quantum mechanics physical quantities are quantized. These quantities are expressed by a number called quantum number. Some quantum numbers related to hydrogen atom are

Principle quantum number n: This quantum number gives information about the energy.

The energy Eigen values of hydrogen atom is

$$E_n = -\frac{me^4}{2n^2\hbar^2}$$

Here n is principle quantum number. $n = 1,2,3 \ldots \ldots$Such that $n \geq l + 1$

Here l is orbital quantum number.

Orbital quantumnumber$\boldsymbol{l}$: This quantum number gives information about orbit's shape.

This quantum number arises by solving $\boldsymbol{\theta_{lm}}$equation for the hydrogen atom. It is represented by $\boldsymbol{l}$.Here $l = 0,1,2 \ldots\ldots (n-1)$ Such that$l \geq |m|$.$m$is called magnetic orbital quantum number.

Magnetic Orbital quantum number$\boldsymbol{m}$: This quantum number gives information about the space orientation of the orbit. This quantum number arises by solving the $\boldsymbol{\phi_m}$equation for the hydrogen atom.It is represented by $\boldsymbol{m}$and$\mathbf{m} = 0, \pm 1, \pm 2, - - -$

Degeneracy

The wave function having same energy are called degenerate wave functions are degenerate states. The number of wave functions having same energy is called degree of degeneracy. All energy levels except n=1 are degenrate.in case of wave functions of one electron atom such as hydrogen degeneracy is n^2. Where n is the principle quantum number. For each n there are n possible values of orbital quantum number l. That is

$l \leq n - 1$.the degree of degeneracy for different orbits is

If n=1 l=0 m=0 degree of degeneracy =2l+1=1=1^2

If n=2 l=0, 1 m= 0, 1) degree of degeneracy =2l+1=1,2l+1=3 that is 3+1=4=2^2

If n=3 l=0, 1,2 m= (0, 1,2) degree of degeneracy =2(0)+1=1,2(1)+1=3,(0)+1=1,2(2)+1=5 that is 5+3+1=9=3^2

So generally degree of degeneracy =1^2,2^2,3^3, --------=n^2

Schrodinger's equation for rigid rotor

Rigid rotor is a system two bodies of mass m_1 and m_2 separated by a finite fixed distance and capable to rotate about their center of mass. Diatomic molecule is the example of rigid rotor. We solve Schrodinger's equation for this rotor.

The kinetic energy of rotor is

$$T = \frac{p^2}{2\mu} \text{ ------- (1)}$$

Here μ is reduced mass where $\mu = \frac{m_1 m_2}{m_1 + m_2}$

As rotor moves freely so potential energy will be

$$V = 0 \text{ -------- (2)}$$

Hamiltonian operator will be

$$H = T + V$$

$$H = \frac{p^2}{2\mu} + 0$$

As $p^2 = -\hbar^2 \nabla^2$ so

$$H = \frac{-\hbar^2 \nabla^2}{2\mu} \text{ ------- (3)}$$

Now the Schrodinger's equation in Cartesian coordinates is

$$\nabla^2 \psi(\mathrm{r}) + \frac{2\mu E}{\hbar^2} \psi(\mathrm{r}) = 0$$

If I is moment of inertia $I = \mu r^2$ so $\mu = \frac{I}{r^2}$

$$\nabla^2 \psi(\mathrm{r}) + \frac{2IE}{r^2 \hbar^2} \psi(\mathrm{r}) = 0 \text{ ------- (4)}$$

We express the Schrodinger's equation in term of spherical coordinates (r, θ, ϕ).

Now ∇^2 in spherical polar coordinates is

$$\nabla^2 = \frac{1}{r^2} \frac{\eth}{\eth r} \left(r^2 \frac{\eth}{\eth r} \right) + \frac{1}{r^2 \sin\theta} \frac{\eth}{\eth \theta} \left(\sin\theta \frac{\eth}{\eth \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\eth^2}{\eth \phi^2}$$

And $$\psi(\mathrm{r}) = \psi = \psi(\mathrm{r}, \theta, \phi)$$

Now Schrodinger's equation 4 will become

$$\frac{1}{r^2} \frac{\eth}{\eth r} \left(r^2 \frac{\eth \psi}{\eth r} \right) + \frac{1}{r^2 \sin\theta} \frac{\eth}{\eth \theta} \left(\sin\theta \frac{\eth \psi}{\eth \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\eth^2 \psi}{\eth \phi^2} + \frac{2IE}{r^2 \hbar^2} \psi = 0$$

$\frac{r^2}{r^2}\frac{\eth}{\eth r}\left(r^2\frac{\eth\psi}{\eth r}\right)+\frac{r^2}{r^2\sin\theta}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\psi}{\eth\theta}\right)+\frac{1}{\sin^2\theta}\frac{\eth^2\psi}{\eth\phi^2}+\frac{2IE}{\hbar^2}\psi=0$ ------- (5)

Since there is no motion along radial direction so $\psi(\mathrm{r},\theta,\phi)=\psi(\theta,\phi)$ so we omit radial component in above equation

$\frac{1}{\sin\theta}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\psi}{\eth\theta}\right)+\frac{1}{\sin^2\theta}\frac{\eth^2\psi}{\eth\phi^2}+\frac{2IE}{\hbar^2}\psi=0$ ------- (6)

We solve equation 5 by variable separation method such that

$$\psi(\theta,\phi)=\boldsymbol{\theta}(\theta)\boldsymbol{\Phi}(\Phi)=\boldsymbol{\theta}\boldsymbol{\Phi}$$

So above equation will be

$$\frac{1}{\sin\theta}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\boldsymbol{\theta}\boldsymbol{\Phi}}{\eth\theta}\right)+\frac{1}{\sin^2\theta}\frac{\eth^2\boldsymbol{\theta}\boldsymbol{\Phi}}{\eth\phi^2}+\frac{2IE}{\hbar^2}\boldsymbol{\theta}\boldsymbol{\Phi}=0$$

$$\frac{\boldsymbol{\Phi}}{\sin\theta}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\boldsymbol{\theta}}{\eth\theta}\right)+\frac{\boldsymbol{\theta}}{\sin^2\theta}\frac{\eth^2\boldsymbol{\Phi}}{\eth\phi^2}+\frac{2IE}{\hbar^2}=0$$

$$\frac{\sin\theta}{\boldsymbol{\theta}}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\boldsymbol{\theta}}{\eth\theta}\right)+\frac{\mathbf{1}}{\boldsymbol{\Phi}}\frac{\eth^2\boldsymbol{\Phi}}{\eth\phi^2}+\frac{2IE\sin^2\theta}{\hbar^2}=0$$

$$\frac{\sin\theta}{\boldsymbol{\theta}}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\boldsymbol{\theta}}{\eth\theta}\right)+\frac{2IE\sin^2\theta}{\hbar^2}=-\frac{\mathbf{1}}{\boldsymbol{\Phi}}\frac{\eth^2\boldsymbol{\Phi}}{\eth\phi^2}$$

In this above equation right side is a function of $\boldsymbol{\Phi}$ while left side is the function of $\boldsymbol{\theta}$**.**So bothare equal to some constant sayλ. Here m^2

In this equation right side is the function of $\boldsymbol{\Phi}$and left side is the function of $\boldsymbol{\theta}$**.** So both areequal to some constantm^2.

$$\frac{\sin\theta}{\boldsymbol{\theta}}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\boldsymbol{\theta}}{\eth\theta}\right)+\frac{2IE\sin^2\theta}{\hbar^2}=-\frac{\mathbf{1}}{\boldsymbol{\Phi}}\frac{\eth^2\boldsymbol{\Phi}}{\eth\phi^2}=m^2$$

That is

$\frac{\sin\theta}{\boldsymbol{\theta}}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\boldsymbol{\theta}}{\eth\theta}\right)+\frac{2IE\sin^2\theta}{\hbar^2}=\mathrm{m}^2$ -------(C)

And

$\frac{\mathbf{1}}{\mathbf{\Phi}}\frac{\eth^2\mathbf{\Phi}}{\eth\phi^2} = -\mathrm{m}^2$ ------- (D)

Equation C and D are the equation of $\boldsymbol{\theta}$and$\mathbf{\Phi}$respectively.

Solution of$\mathbf{\Phi}$ equation D

As$\frac{\mathbf{1}}{\mathbf{\Phi}}\frac{\eth^2\mathbf{\Phi}}{\eth\phi^2} = -\mathrm{m}^2$

$$\frac{\eth^2\mathbf{\Phi}}{\eth\phi^2} = -\mathrm{m}^2\mathbf{\Phi}$$

$$\frac{\eth^2\mathbf{\Phi}}{\eth\phi^2} + \mathrm{m}^2\mathbf{\Phi} = 0$$

This is second order differential equation whose solution is

$$\mathbf{\Phi} = \Phi_o e^{im\phi}$$

Here $\mathrm{m} = 0, \pm1, \pm2, - - -$ and Φ_o is constant.

The normalized wave function will be

$$\mathbf{\Phi} = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

Solution of$\boldsymbol{\theta}$ equation C

As θ equation is

$$\frac{\sin\theta}{\boldsymbol{\theta}}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\boldsymbol{\theta}}{\eth\theta}\right) + \frac{2IE\sin^2\theta}{\hbar^2} - \mathrm{m}^2 = 0$$

$$\sin\theta\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\boldsymbol{\theta}}{\eth\theta}\right) + (\frac{2IE\sin^2\theta}{\hbar^2} - \mathrm{m}^2)\boldsymbol{\theta} = 0$$

$$\frac{1}{\sin\theta}\frac{\eth}{\eth\theta}\left(\sin\theta\frac{\eth\boldsymbol{\theta}}{\eth\theta}\right) + (\frac{2IE}{\hbar^2} - \frac{\mathrm{m}^2}{\sin^2\theta})\boldsymbol{\theta} = 0$$

This is special type of differential equation. We solve it by substitution method.

$$\text{Let } x = \cos\theta$$

$$\frac{\eth}{\eth\theta} = \frac{\eth}{\eth x}\frac{\eth x}{\eth\theta} = -\sin\theta\frac{\eth}{\eth x}$$

So above equation will become

$$\frac{1}{\sin\theta}\left(-\sin\theta\frac{\eth}{\eth x}\right)\left(\sin\theta\left(-\sin\theta\frac{\eth}{\eth x}\right)\boldsymbol{\theta}\right)+\left\{\frac{2IE}{\hbar^2}-\frac{\mathrm{m}^2}{1-\cos^2\theta}\right\}\boldsymbol{\theta}=0$$

$$\frac{\eth}{\eth x}\left(\sin^2\theta\frac{\eth\boldsymbol{\theta}}{\eth x}\right)+\left\{\frac{2IE}{\hbar^2}-\frac{\mathrm{m}^2}{1-\cos^2\theta}\right\}\boldsymbol{\theta}=0$$

$$\frac{\eth}{\eth x}\left((1-\cos^2\theta)\frac{\eth\boldsymbol{\theta}}{\eth x}\right)+\left\{\frac{2IE}{\hbar^2}-\frac{\mathrm{m}^2}{1-\cos^2\theta}\right\}\boldsymbol{\theta}=0$$

$$\frac{\eth}{\eth x}\left((1-x^2)\frac{\eth\boldsymbol{\theta}}{\eth x}\right)+\left\{\frac{2IE}{\hbar^2}-\frac{\mathrm{m}^2}{1-x^2}\right\}\boldsymbol{\theta}=0$$

$$(1-x^2)\frac{\eth^2\boldsymbol{\theta}}{\eth x^2}-2x\frac{\eth\boldsymbol{\theta}}{\eth x}+\left\{\frac{2IE}{\hbar^2}-\frac{\mathrm{m}^2}{1-x^2}\right\}\boldsymbol{\theta}=0$$

If $\frac{2IE}{\hbar^2}=l(l+1)$

$$(1-x^2)\frac{\eth^2\boldsymbol{\theta}}{\eth x^2}-2x\frac{\eth\boldsymbol{\theta}}{\eth x}+\left\{l(l+1)-\frac{\mathrm{m}^2}{1-x^2}\right\}\boldsymbol{\theta}=0$$

This is associated Legendre's polynomial equation whose solution is

$$P_l^m=\frac{(1-x^2)^{\frac{m}{2}}}{2^l l!}\frac{\eth^{m+l}}{\eth x^{m+l}}(x^2-1)^l$$

Some associated Legendre polynomials are

$$P_0^0(x)=1\ \ or\quad P_0^0(cos\theta)=1$$

$$P_1^1(x)=(1-x^2)^{\frac{1}{2}}\ \ or\quad P_1^1(cos\theta)=sin\theta$$

$$P_2^1(x)=3x(1-x^2)^{\frac{1}{2}}\ \ or\quad P_2^1(cos\theta)=3cos\theta sin\theta$$

$$P_2^2(x)=3(1-x^2)\ or\quad P_2^2(cos\theta)=3sin^2\theta$$

$$P_3^1(x)=\frac{3}{2}(5x^2-1)(1-x^2)^{\frac{1}{2}}\ or\quad P_3^1(cos\theta)=\frac{3}{2}(5cos^2\theta-1)sin\theta$$

$$P_3^2(x)=15x(1-x^2)\ or\quad P_3^2(cos\theta)=15cos\theta sin^2\theta$$

$$P_3^3(x)=15x(1-x^2)^{\frac{3}{2}}\ or\quad P_3^3(cos\theta)=15sin^3\theta$$

Now the solution of $\boldsymbol{\theta}$ equation will be

$$\boldsymbol{\theta_{lm}} = \sqrt{\frac{(2l+1)(l-m)!}{2\pi(lm)!}} P_l^m(cos\theta)$$

The complete wave function will be

$$\psi(\theta,\phi) = \boldsymbol{\theta\Phi} = \sqrt{\frac{(2l+1)(l-m)!}{2\pi(lm)!}} P_l^m(cos\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

CHAPTER 8

APPROXIMATION TECHNIQUES

Perturbation

In quantum mechanics some problems have exact solutions such as particle in a box,

Particle in a well, hydrogen atom and harmonic oscillator etc. If we slightly disturb the system than exact solution become difficult. So we need an approximate solution. Perturbation is a technique to get an approximate solution.

Types

Perturbation has two types

1. Time independent perturbation theory
2. Time dependent perturbation theory

1. Time independent perturbation theory

In this approximation we only focus on position, energy and momentum etc. and exclude time. It has again two subtypes

1. Non-degenerate perturbation
2. De-generate perturbation

1. Non-degenerate perturbation: we have Schrodinger's equation

$$H_o\psi_o = E_o\psi_o$$

Here $H_o$is Hamiltonian, E_o is ground state energy and ψ_o is ground state wave function.

If we slightly disturb the system the Hamiltonian will become

$$H = H_o + \epsilon H'$$

Here H' is perturbed Hamiltonian and ϵ is constant that gives the strength of perturbation. Where$\epsilon \ll 1$. Now Schrodinger's equation will be written as

$$(H_o + \epsilon H')\psi_n = E_{\boldsymbol{n}}\psi_n \text{ ------- (1)}$$

Since the changes will be very small so we expand the power series of ψ_n and$E_{\boldsymbol{n}}$.

Power series of ψ_n will be

$$\psi_n = \epsilon^0\psi_n^0 + \epsilon^1\psi_n^1 + \epsilon^2\psi_n^2 + \epsilon^3\psi_n^3 - - - -$$

Power series of E_n will be

$$E_n = \epsilon^0 E_n^0 + \epsilon^1 E_n^1 + \epsilon^2 E_n^2 + \epsilon^3 E_n^3 - - - -$$

So we express equation 1 as

$$(\boldsymbol{H_o + \epsilon H'})(\boldsymbol{\epsilon^0\psi_n^0 + \epsilon^1\psi_n^1 + \epsilon^2\psi_n^2 + \epsilon^3\psi_n^3 - - -}) = (\boldsymbol{\epsilon^0 E_n^0 + \epsilon^1 E_n^1 + \epsilon^2 E_n^2 + \epsilon^3 E_n^3 - -})(\boldsymbol{\epsilon^0\psi_n^0 + \epsilon^1\psi_n^1 + \epsilon^2\psi_n^2 + \epsilon^3\psi_n^3 - - -})$$

Compere the coefficient of $\epsilon^0, \epsilon^1, \epsilon^2 - - -$

Coefficient ofϵ^0

$$H_o\psi_n^0 = \boldsymbol{E_n^0}\psi_n^0 \text{ ------- (i)}$$

Coefficient ofϵ^1

$$H_o\psi_n^1 + H'\psi_n^0 = \boldsymbol{E_n^0}\psi_n^1 + \boldsymbol{E_n^1}\psi_n^0 \text{ ------- (ii)}$$

Coefficient ofϵ^2

$$H_o\psi_n^2 + H'\psi_n^1 = \boldsymbol{E_n^0}\psi_n^2 + \boldsymbol{E_n^1}\psi_n^1 + \boldsymbol{E_n^2}\psi_n^0 \text{ ------- (iii)}$$

Higher terms are very small so we neglect them.

Now equation (i) is the solution of unperturbed system. Equation (ii) and (iii) are respectively called first order and second order corrections equations.

Assessment of first order energy correction

Now equation (ii) can be arranged as

$$(H_o - \boldsymbol{E_n^0})\psi_n^1 = (\boldsymbol{E_n^1} - H')\psi_n^0$$

Now ψ_n^1 can be written as

$$\psi_n^1 = \sum_m a_m^1 \, \psi_m^0$$

Put in above equation

$$(H_o - \boldsymbol{E_n^0}) \sum_m a_m^1 \, \psi_m^0 = (\boldsymbol{E_n^1} - H')\psi_n^0$$

$$\sum_m a_m^1 \, H_o \psi_m^0 - \boldsymbol{E_n^0} \sum_m a_m^1 \, \psi_m^0 = (\boldsymbol{E_n^1} - H')\psi_n^0$$

As $H_o \psi_m^0 = \boldsymbol{E_m^0} \psi_m^0$ so

$$\sum_m a_m^1 \boldsymbol{E_m^0} \psi_m^0 - \boldsymbol{E_n^0} \sum_n a_n^1 \, \psi_m^0 = (\boldsymbol{E_n^1} - H')\psi_n^0$$

$$\sum_m a_m^1 \, (\boldsymbol{E_m^0} - \boldsymbol{E_n^0}) \, \psi_m^0 = (\boldsymbol{E_n^1} - H')\psi_n^0$$

Multiply both sides by ψ_n^{*0} and integrate over whole volume

$$\int \sum_m a_m^1 \, (\boldsymbol{E_m^0} - \boldsymbol{E_n^0}) \, \psi_n^{*0} \, \psi_m^0 \, dv = \int \psi_n^{*0} (\boldsymbol{E_n^1} - H')\psi_n^0 dv$$

Using condition of orthonormality

$$\int \psi_n^{*0} \, \psi_m^0 \, dv = \begin{cases} 1 & if \; m = n \\ 0 & if \; m \neq n \end{cases}$$

For the case $m \neq n$ we get

$$0 = \int \psi_n^{*0} (\boldsymbol{E_n^1} - H')\psi_n^0 dv$$

$$\int \psi_n^{*0} \boldsymbol{E_n^1} \, \psi_n^0 dv = \int \psi_n^{*0} H' \psi_n^0 dv$$

As $\int \psi_n^{*0} \boldsymbol{E_n^1} \psi_n^0 dv = \int \boldsymbol{E_n^1} \psi_n^{*0} \psi_n^0 dv = \boldsymbol{E_n^1}$ Using condition of orthonormality

So $\boldsymbol{E_n^1} = \int \psi_n^{*0} H' \psi_n^0 dv$

Or $\boldsymbol{E_n^1} =< \psi_n^{*0} / H' / \psi_n^0 >=< n / H' / n >$

This is first order energy correction.

Assessment of first order correction to wave function

Now again we take the equation

$$\sum_m a_m^1 (\boldsymbol{E_m^0} - \boldsymbol{E_n^0}) \psi_m^0 = (\boldsymbol{E_n^1} - H') \psi_n^0$$

Multiply both sides by ψ_m^{*0} and integrate over whole volume

$$\int \sum_m a_m^1 (\boldsymbol{E_m^0} - \boldsymbol{E_n^0}) \psi_m^{*0} \psi_m^0 \, dv = \int \psi_m^{*0} (\boldsymbol{E_n^1} - H') \psi_n^0 dv$$

Using condition of orthonormality

$$\sum_m a_m^1 (\boldsymbol{E_m^0} - \boldsymbol{E_n^0}) = \int \boldsymbol{E_n^1} \psi_m^{*0} \psi_n^0 dv - \int \psi_m^{*0} H' \psi_n^0 dv$$

$$\sum_m a_m^1 = \frac{-\int \psi_m^{*0} H' \psi_n^0 dv}{(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})}$$

$$\sum_m a_m^1 = \frac{\int \psi_m^{*0} H' \psi_n^0 dv}{(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})}$$

$$\sum_m a_m^1 = \frac{< \psi_m^{*0} / H' / \psi_n^0 >}{(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})}$$

$$\sum_m a_m^1 = \frac{< m / H' / n >}{(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})}$$

So first order correction to wave function will become

$$\psi_n^1 = \sum_m a_m^1 \psi_m^0$$

$$\psi_n^1 = \frac{< m / H' / n >}{(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})} \psi_m^0$$

Assessment of second order energy correction

Now we take equation (iii)

$$H_o\psi_n^2 + H'\psi_n^1 = \boldsymbol{E_n^0}\psi_n^2 + \boldsymbol{E_n^1}\psi_n^1 + \boldsymbol{E_n^2}\psi_n^0$$

We arrange it

$$H_o\psi_n^2 - \boldsymbol{E_n^0}\psi_n^2 = (\boldsymbol{E_n^1} - H')\psi_n^1 + \boldsymbol{E_n^2}\psi_n^0$$

Now ψ_n^1 and ψ_n^2can be written as

$$\psi_n^1 = \sum_m a_m^1\,\psi_m^0$$

$$\psi_n^2 = \sum_m a_m^2\,\psi_m^0$$

Use these values in above equation

$$\sum_m a_m^2 H_o\,\psi_m^0 - \sum_m a_m^2 \boldsymbol{E_n^0}\,\psi_m^0 = \sum_m a_m^1(\boldsymbol{E_n^1} - H')\,\psi_m^0 + \boldsymbol{E_n^2}\psi_n^0$$

As $H_o\,\psi_m^0 = \boldsymbol{E_m^0}\,\psi_m^0$ there fore

$$\sum_m a_m^2 \boldsymbol{E_m^0}\,\psi_m^0 - \sum_m a_m^2 \boldsymbol{E_n^0}\,\psi_m^0 = \sum_m a_m^1(\boldsymbol{E_n^1} - H')\,\psi_m^0 + \boldsymbol{E_n^2}\psi_n^0$$

$$\sum_m a_m^2(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})\psi_m^0 = \sum_m a_m^1(\boldsymbol{E_n^1} - H')\,\psi_m^0 + \boldsymbol{E_n^2}\psi_n^0$$

Multiply both sides by ψ_n^{*0} and integrate over whole volume

$$\int \sum_m a_m^2(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})\,\psi_n^{*0}\psi_m^0\,dv = \int \sum_m a_m^1\,\psi_n^{*0}(\boldsymbol{E_n^1} - H')\,\psi_m^0\,dv + \int \boldsymbol{E_n^2}\,\psi_n^{*0}\psi_n^0\,dv$$

$$\int \sum_m a_m^2(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})\,\psi_n^{*0}\psi_m^0\,dv = \int \sum_m a_m^1\,\psi_n^{*0}\boldsymbol{E_n^1}\,\psi_m^0\,dv - \int \sum_m a_m^1\,\psi_n^{*0}H'\,\psi_m^0\,dv + \int \boldsymbol{E_n^2}\,\psi_n^{*0}\psi_n^0\,dv$$

Using condition of orthonormality

$$\int \psi_n^{*0}\,\psi_m^0\,dv = \begin{cases} 1 & if\ m = n \\ 0 & if\ m \neq n \end{cases}$$

For the case $m \neq n$ we get

$$0 = -\int \sum_m a_m^1 \, \psi_n^{*0} H' \, \psi_m^0 \, dv + \boldsymbol{E_n^2}$$

$$\boldsymbol{E_n^2} = \int \sum_m a_m^1 \, \psi_n^{*0} H' \, \psi_m^0 \, dv$$

But

$$\sum_m a_m^1 = \frac{\int \psi_m^{*0} \, H' \psi_n^0 dv}{(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})}$$

So

$$\boldsymbol{E_n^2} = \frac{\int \psi_m^{*0} \, H' \psi_n^0 dv}{(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})} \int \psi_n^{*0} H' \, \psi_m^0 \, dv$$

$$\boldsymbol{E_n^2} = \frac{< m \, / H' / \, n >}{(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})} < n \, / H' / \, m >$$

$$\boldsymbol{E_n^2} = \frac{< m \, / H' / \, n >< n \, / H' / \, m >}{(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})}$$

This is second order energy correction.

Assessment of second order correction to wave function

Now again we take the equation

$$\sum_m a_m^2 (\boldsymbol{E_m^0} - \boldsymbol{E_n^0}) \psi_m^0 = \sum_m a_m^1 (\boldsymbol{E_n^1} - H') \, \psi_m^0 + \boldsymbol{E_n^2} \psi_n^0$$

Multiply both sides by ψ_m^{*0} and integrate over whole volume

$$\int \sum_m a_m^2 (\boldsymbol{E_m^0} - \boldsymbol{E_n^0}) \, \psi_m^{*0} \psi_m^0 \, dv = \int \sum_m a_m^1 \, \psi_m^{*0} (\boldsymbol{E_n^1} - H') \, \psi_m^0 \, dv + \int \psi_m^{*0} \psi_n^0 dv \, \boldsymbol{E_n^2}$$

Using condition of orthonormality

$$\int \psi_n^{*0} \, \psi_m^0 \, dv = \begin{cases} 1 & if \; m = n \\ 0 & if \; m \neq n \end{cases}$$

For the case $m \neq n$ we get

$$\sum_m a_m^2(\boldsymbol{E_m^0} - \boldsymbol{E_n^0}) = \int \sum_m a_m^1\, \psi_m^{*0}(\boldsymbol{E_n^1} - H')\, \psi_m^0\, dv$$

$$\sum_m a_m^2(\boldsymbol{E_m^0} - \boldsymbol{E_n^0}) = \sum_m a_m^1\, \boldsymbol{E_n^1} - \int \sum_m a_m^1\, \psi_m^{*0} H'\, \psi_m^0\, dv$$

$$\sum_m a_m^2 = \frac{\sum_m a_m^1\, \boldsymbol{E_n^1} - \int \sum_m a_m^1\, \psi_m^{*0} H'\, \psi_m^0\, dv}{(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})}$$

$$\sum_m a_m^2 = \frac{\sum_m a_m^1\, \boldsymbol{E_n^1} - \sum_m a_m^1 < \psi_m^{*0}/H'/\, \psi_m^0 >}{(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})}$$

Use the values of

$$\sum_m a_m^1 = \frac{< m\ /H'/\ n >}{(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})}$$

And $$\boldsymbol{E_n^1} =< \psi_n^{*0}/H'/\psi_n^0 >=< m/H'/m >$$

$$\sum_m a_m^2 = \frac{< m\ /H'/\ n >< n/H'/m >}{(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})} - \frac{< m\ /H'/\ n >< m/H'/m >}{(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})}$$

As second order wave function is

$$\psi_n^2 = \sum_m a_m^2\, \psi_m^0$$

$$\psi_n^2 = \left[\frac{< m\ /H'/\ n >< n/H'/m >}{(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})} - \frac{< m\ /H'/\ n >< m/H'/m >}{(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})}\right] / \psi_m^0 >$$

This is second order correction to wave function.

Now we can write the solution up to second order correction as

$$E_n = \epsilon^0 E_n^0 + \epsilon^1 E_n^1 + \epsilon^2 E_n^2$$

$$E_n = E_n^0 + \epsilon^1 < n/H'/n > + \epsilon^2 \frac{< m\ /H'/\ n >< n\ /H'/\ m >}{(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})}$$

and

$$\psi_n = \psi_n^0 + \epsilon^1 \frac{< m\ /H'/\ n >}{(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})}\ /\psi_m^0 > + \epsilon^2 \left[\frac{< m\ /H'/\ n >< n/H'/m >}{(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})(\boldsymbol{E_n^0} - \boldsymbol{E_m^0})} - \frac{< m\ /H'/\ n >< m/H'/m >}{(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})(\boldsymbol{E_m^0} - \boldsymbol{E_n^0})}\right] / \psi_m^0 >$$

De-generate perturbation

We know that if two or more states have same energy then these states are called degenerate states.

If we look upon the non degenerate purturbatin energy and wave function

$$E_n = E_n^0 + \epsilon^1 < n/H'/n > + \epsilon^2 \frac{< m\ /H'/\ n >< n\ /H'/\ m >}{(\boldsymbol{E_n^0 - E_m^0})}$$

and

$$\psi_n = \psi_n^0 + \epsilon^1 \frac{< m\ /H'/\ n >}{(\boldsymbol{E_n^0 - E_m^0})}\ /\psi_m^0 > + \epsilon^2 \left[\frac{< m\ /H'/\ n >< n/H'/m >}{(\boldsymbol{E_m^0 - E_n^0})(E_n^0 - E_m^0)} - \frac{< m\ /H'/\ n >< m/H'/m >}{(\boldsymbol{E_m^0 - E_n^0})(E_m^0 - E_n^0)}\right] / \psi_m^0 >$$

If $\boldsymbol{E_m^0 = E_n^0}$ Then $E_n \to \infty$ and $\psi_n \to \infty$

So non degenerate perturbation theory, remain no more useful.

So for the case when $\boldsymbol{E_m^0 = E_n^0}$ **,** Degenerate perturbation theory arrived.

Let $\psi_1^0\ and\ \psi_2^0$ are two unperturbed degenerate states with energy $\boldsymbol{E_n^0}$**. If** H_o is unperturbed Hamiltonian then we can write

$$H_o\psi_1^0 = \boldsymbol{E_n^0}\psi_1^0$$

And

$$H_o\psi_2^0 = \boldsymbol{E_n^0}\psi_2^0$$

Their linear combination will be

$$\psi_n^0 = \boldsymbol{a}\psi_1^0 + b\psi_2^0$$

If we slightly disturb the system the Hamiltonian will become

$$H = H_o + \epsilon H'$$

Here H' is perturbed Hamiltonian and ϵ is constant that gives the strength of perturbation. Where $\epsilon \ll 1$. Now Schrodinger's equation will be written as

$$(H_o + \epsilon H')\psi_n = \boldsymbol{E_n}\psi_n \text{ ------- (1)}$$

Since the changes will be very small so we expand the power series of ψ_n and$\boldsymbol{E_n}$**.**

Power series of ψ_n will be

$$\psi_n = \epsilon^0\psi_n^0 + \epsilon^1\psi_n^1 + \epsilon^2\psi_n^2 + \epsilon^3\psi_n^3 - - - -$$

Power series of E_n will be

$$E_n = \epsilon^0 E_n^0 + \epsilon^1 E_n^1 + \epsilon^2 E_n^2 + \epsilon^3 E_n^3 - - - -$$

So we express equation 1 as

$$(\boldsymbol{H_o} + \boldsymbol{\epsilon H'})(\boldsymbol{\epsilon^0 \psi_n^0} + \boldsymbol{\epsilon^1 \psi_n^1} + \boldsymbol{\epsilon^2 \psi_n^2} + \boldsymbol{\epsilon^3 \psi_n^3} - --) = (\boldsymbol{\epsilon^0 E_n^0} + \boldsymbol{\epsilon^1 E_n^1} + \boldsymbol{\epsilon^2 E_n^2} + \boldsymbol{\epsilon^3 E_n^3} - -)(\boldsymbol{\epsilon^0 \psi_n^0} + \boldsymbol{\epsilon^1 \psi_n^1} + \boldsymbol{\epsilon^2 \psi_n^2} + \boldsymbol{\epsilon^3 \psi_n^3} - --)$$

Compere the coefficient of $\epsilon^0, \epsilon^1, \epsilon^2 - - -$

Coefficient ofϵ^0

$$H_o \psi_n^0 = \boldsymbol{E_n^0} \psi_n^0 \quad \text{------- (i)}$$

Coefficient ofϵ^1

$$H_o \psi_n^1 + H' \psi_n^0 = \boldsymbol{E_n^0} \psi_n^1 + \boldsymbol{E_n^1} \psi_n^0 \quad \text{------- (ii)}$$

Coefficient ofϵ^2

$$H_o \psi_n^2 + H' \psi_n^1 = \boldsymbol{E_n^0} \psi_n^2 + \boldsymbol{E_n^1} \psi_n^1 + \boldsymbol{E_n^2} \psi_n^0 \quad \text{------- (iii)}$$

Higher terms are very small so we neglect them.

Now equation (i) is the solution of unperturbed system. Equation (ii) and (iii) are respectively called first order and second order corrections equations.

Assessment of first order energy correction

Now equation (ii) can be arranged as

$$H_o \psi_n^1 + H' \psi_n^0 = \boldsymbol{E_n^0} \psi_n^1 + \boldsymbol{E_n^1} \psi_n^0$$

Multiply both sides by ψ_1^0 and integrate over whole volume

$$\int \psi_1^0 H_o \psi_n^1 \, dv + \int \psi_1^0 H' \psi_n^0 \, dv = \int \psi_1^0 \boldsymbol{E_n^0} \psi_n^1 dv + \int \psi_1^0 \boldsymbol{E_n^1} \psi_n^0 \, dv$$

$$\int \psi_1^0 \boldsymbol{E_n^0} \psi_n^1 \, dv + \int \psi_1^0 H' \psi_n^0 \, dv = \int \psi_1^0 \boldsymbol{E_n^0} \psi_n^1 dv + \int \psi_1^0 \boldsymbol{E_n^1} \psi_n^0 \, dv$$

$$\int \psi_1^0 H' \psi_n^0 \, dv = \int \psi_1^0 \boldsymbol{E_n^1} \psi_n^0 \, dv$$

As

$$\psi_n^0 = \boldsymbol{a}\psi_1^0 + b\psi_2^0$$

So

$$\int \psi_1^0 H'(\boldsymbol{a}\psi_1^0 + b\psi_2^0)\, dv = \int \boldsymbol{E_n^1}\, \psi_1^0(\boldsymbol{a}\psi_1^0 + b\psi_2^0)\, dv$$

$$a\int \psi_1^0 H'\psi_1^0 dv + b\int \psi_1^0 H'\psi_2^0\, dv = a\int \boldsymbol{E_n^1}\, \psi_1^0\psi_1^0 dv + b\int \boldsymbol{E_n^1}\, \psi_1^0\psi_2^0 dv$$

$$a\int \psi_1^0 H'\psi_1^0 dv + b\int \psi_1^0 H'\psi_2^0\, dv = a\boldsymbol{E_n^1}$$

$$a < \psi_1^0/H'/\psi_1^0 > + b < \psi_1^0/H'/\psi_2^0 >= a\boldsymbol{E_n}$$

$$a(H')_{11} + b(H')_{12} = a\boldsymbol{E_n^1} \text{ ---------- (A)}$$

Similarly Multiply equation(ii) both sides by ψ_2^0 and integrate over whole volume

$$\int \psi_2^0 H_o\psi_n^1\, dv + \int \psi_2^0 H'\psi_n^0\, dv = \int \psi_2^0 \boldsymbol{E_n^0}\psi_n^1 dv + \int \psi_2^0 \boldsymbol{E_n^1}\psi_n^0\, dv$$

$$\int \psi_2^0 \boldsymbol{E_n^0}\psi_n^1\, dv + \int \psi_2^0 H'\psi_n^0\, dv = \int \psi_2^0 \boldsymbol{E_n^0}\psi_n^1 dv + \int \psi_2^0 \boldsymbol{E_n^1}\psi_n^0\, dv$$

$$\int \psi_2^0 H'\psi_n^0\, dv = \int \psi_2^0 \boldsymbol{E_n^1}\psi_n^0\, dv$$

As

$$\psi_n^0 = \boldsymbol{a}\psi_1^0 + b\psi_2^0$$

So

$$\int \psi_2^0 H'(\boldsymbol{a}\psi_1^0 + b\psi_2^0)\, dv = \int \boldsymbol{E_n^1}\, \psi_2^0(\boldsymbol{a}\psi_1^0 + b\psi_2^0)\, dv$$

$$a\int \psi_2^0 H'\psi_1^0 dv + b\int \psi_2^0 H'\psi_2^0\, dv = a\int \boldsymbol{E_n^1}\, \psi_2^0\psi_1^0 dv + b\int \boldsymbol{E_n^1}\, \psi_2^0\psi_2^0 dv$$

$$a\int \psi_2^0 H'\psi_1^0 dv + b\int \psi_2^0 H'\psi_2^0\, dv = b\boldsymbol{E_n^1}$$

$$a < \psi_2^0/H'/\psi_1^0 > + b < \psi_2^0/H'/\psi_2^0 >= b\boldsymbol{E_n^1}$$

$$a(H')_{21} + b(H')_{22} = b\boldsymbol{E_n^1} \text{ ---------- (B)}$$

From equation (A)

$$b(H')_{12} = a(\boldsymbol{E_n^1} - (H')_{11})$$

$$a = \frac{b(H')_{12}}{(\boldsymbol{E_n^1} - (H')_{11}}$$

Substitute value of a in equation (B)

$$\frac{b(H')_{12}}{(\boldsymbol{E_n^1} - (H')_{11}}(H')_{21} + b(H')_{22} = b\boldsymbol{E_n}$$

$$(H')_{12}(H')_{21} + (\boldsymbol{E_n^1} - (H')_{11})(H')_{22} = (\boldsymbol{E_n^1} - (H')_{11})\boldsymbol{E_n^1}$$

$$(H')_{12}(H')_{21} + \boldsymbol{E_n^1}(H')_{22} - (H')_{11}(H')_{22} = \boldsymbol{E_n^1}\boldsymbol{E_n^1} - (H')_{11})\boldsymbol{E_n^1}$$

$$(\boldsymbol{E_n^1})^2 - \boldsymbol{E_n^1}\{(H')_{11} + (H')_{22}\} + (H')_{11}(H')_{22} - (H')_{11}(H')_{21} = 0$$

This is quadratic equation whose solution is

$$\boldsymbol{E_n^1} = \frac{\{(\boldsymbol{H'})_{11} + (\boldsymbol{H'})_{22}\} \pm \sqrt{\{(\boldsymbol{H'})_{11} + (\boldsymbol{H'})_{22}\}^2 - 4(\boldsymbol{H'})_{11}(\boldsymbol{H'})_{22} - (\boldsymbol{H'})_{11}(\boldsymbol{H'})_{21}}}{2}$$

This equation shows $\boldsymbol{E_n^1}$ has two solutions

1. $\boldsymbol{E_n^1} = \frac{\{(\boldsymbol{H'})_{11} + (\boldsymbol{H'})_{22}\} + \sqrt{\{(\boldsymbol{H'})_{11} + (\boldsymbol{H'})_{22}\}^2 - 4(\boldsymbol{H'})_{11}(\boldsymbol{H'})_{22} - (\boldsymbol{H'})_{11}(\boldsymbol{H'})_{21}}}{2}$
2. $\boldsymbol{E_n^1} = \frac{\{(\boldsymbol{H'})_{11} + (\boldsymbol{H'})_{22}\} - \sqrt{\{(\boldsymbol{H'})_{11} + (\boldsymbol{H'})_{22}\}^2 - 4(\boldsymbol{H'})_{11}(\boldsymbol{H'})_{22} - (\boldsymbol{H'})_{11}(\boldsymbol{H'})_{21}}}{2}$

This implies that under perturbation, state is no longer degenerate.

We can also solve equation (A) and (B) by matrix algebra

Re-writing the equations (A) and (B)

$$a(H')_{11} + b(H')_{12} = a\boldsymbol{E_n^1} \text{ ---------- (A)}$$

$$a(H')_{21} + b(H')_{22} = b\boldsymbol{E_n^1} \text{ ---------- (B)}$$

By matrix

$$\begin{pmatrix}(H')_{11} & (H')_{12}\\ (H')_{21} & 1(H')_{22}\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} = \boldsymbol{E_n^1}\begin{pmatrix}a\\ b\end{pmatrix}$$

Now eigen value equation is

$$\det (A-\lambda I)=0$$

$$\begin{vmatrix}(H')_{11} - \boldsymbol{E_n^1} & (H')_{12}\\ (H')_{21} & (H')_{22}-\boldsymbol{E_n^1}\end{vmatrix} = 0$$

$$((H')_{11} - \boldsymbol{E_n^1})((H')_{22}-\boldsymbol{E_n^1}) - (H')_{21}(H')_{12} = 0$$

$$(H')_{11}(H')_{12} - (H')_{11}\boldsymbol{E_n^1} - \boldsymbol{E_n^1}(H')_{22} + \boldsymbol{E_n^{1^2}} - (H')_{21}(H')_{12} = 0$$

$$(\boldsymbol{E_n^1})^2 - \boldsymbol{E_n^1}\{(H')_{11} + (H')_{22}\} + (H')_{11}(H')_{22} - (H')_{11}(H')_{21} = 0$$

This is now again quadratic equation whose solution already has obtained above.

Note two fold degenerate states we solve two equations, for three fold we solve three equations and for n-fold degeneracy we solve n equations.

For n-fold degeneracy

$$\begin{vmatrix}(H')_{11} - \boldsymbol{E_n^1} & (H')_{12} & \cdots (H')_{1n}\\ (H')_{21} & (H')_{22}-\boldsymbol{E_n^1} & \cdots (H')_{2n}\\ \vdots & \vdots & \vdots\\ (H')_{n1} & (H')_{n2} & \cdots (H')_{nn}-\boldsymbol{E_n^1}\end{vmatrix} = 0$$

Time dependent perturbation Theory

When the both Hamiltonian of the system and wave functions are time dependent then we solve the perturbation problems by using time dependent perturbation.

Now we start from Schrödinger's equation

$$H_o\Psi_o = i\hbar\frac{\partial\Psi_o}{\partial t}$$

Here $\boldsymbol{\Psi_o}$ and $\boldsymbol{H_o}$ are the wave function and Hamiltonian of the free particle. In the presence of interaction potential or perturbation $\boldsymbol{H'(x,t)}$

$$H = H_o + H^{'}(x,t)$$

Now as time dependent wave function is

$$\Psi(t) = \sum_n a_n(t)\,\Psi_n(x) e^{\frac{-iE_n t}{\hbar}}$$

Now Schrodinger equation become

$$H\Psi(t) = i\hbar \frac{\partial \Psi(t)}{\partial t}$$

$$(H_o + H^{'}(x,t)) \sum_n a_n(t)\,\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} = i\hbar \frac{\partial}{\partial t}\{\sum_n a_n(t)\,\Psi_n(x) e^{\frac{-iE_n t}{\hbar}}\}$$

$$(H_o + H^{'}(x,t)) \sum_n a_n(t)\,\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} = i\hbar \sum_n \frac{da_n(t)}{dt}\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} + i\hbar \sum_n a_n(t)\Psi_n(x) \frac{de^{\frac{-iE_n t}{\hbar}}}{dt}$$

$$(H_o + H^{'}(x,t)) \sum_n a_n(t)\,\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} = i\hbar \sum_n \frac{da_n(t)}{dt}\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} + i\hbar \sum_n a_n(t)\Psi_n(x)\, e^{\frac{-iE_n t}{\hbar}} (\frac{-iE_n}{\hbar})$$

$$H_o \sum_n a_n(t)\,\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} + H^{'}(x,t) \sum_n a_n(t)\,\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} = i\hbar \sum_n \frac{da_n(t)}{dt}\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} + E_n \sum_n a_n(t)\Psi_n(x)\, e^{\frac{-iE_n t}{\hbar}}$$

As $H_o \Psi_n(x) = E_n \Psi_n(x)$

$$E_n \sum_n a_n(t)\Psi_n(x)\, e^{\frac{-iE_n t}{\hbar}} + H^{'}(x,t) \sum_n a_n(t)\,\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} = i\hbar \sum_n \frac{da_n(t)}{dt}\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} + E_n \sum_n a_n(t)\Psi_n(x)\, e^{\frac{-iE_n t}{\hbar}}$$

$$i\hbar \sum_n \frac{da_n(t)}{dt}\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} = H'(x,t) \sum_n a_n(t)\,\Psi_n(x) e^{\frac{-iE_n t}{\hbar}}$$

Multiply by $\Psi_m{}^*(x)$ and integrate

$$\int i\hbar \sum_n \frac{da_n(t)}{dt}\Psi_m{}^*(x)\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} dx = \int \sum_n a_n(t)\Psi_m{}^*(x) H'(x,t)\,\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} dx$$

At left side if n=m

$$\int i\hbar \sum_n \frac{da_m(t)}{dt}\Psi_m(x)\Psi_m(x) e^{\frac{-iE_m t}{\hbar}} dx = \int \sum_n a_n(t)\Psi_m{}^*(x) H'(x,t)\,\Psi_n(x) e^{\frac{-iE_n t}{\hbar}} dx$$

$$i\hbar \sum_n \frac{da_m(t)}{dt} e^{\frac{-iE_m t}{\hbar}} = \sum_n a_n(t) < m/H'/n > e^{\frac{-iE_n t}{\hbar}}$$

$$\frac{da_m(t)}{dt} = -\frac{i}{\hbar} \sum_n a_n(t) < m/H'/n > e^{\frac{i(E_m - E_n)t}{\hbar}}$$

$$\frac{da_m(t)}{dt} = -\frac{i}{\hbar} \sum_n a_n(t) < m/H'/n > e^{i\omega_{mn} t}$$

In matrix form

$$\begin{pmatrix} \frac{da_m{}^1(t)}{dt} \\ \frac{da_m{}^2(t)}{dt} \\ \vdots \end{pmatrix} = -\frac{i}{\hbar} \begin{pmatrix} H'_{11} & H'_{12} e^{i\omega_{12} t} & \cdots \\ H'_{21} e^{i\omega_{21} t} & H'_{22} & \cdots \\ \cdots & \cdots & H'_{33} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix}$$

Or we can expand the summation on right side

$$\frac{da_m(t)}{dt} = \sum_{m=n} -\frac{i}{\hbar} H' e^{i\omega_{mn} t} - \frac{i}{\hbar} \sum_{n \neq m} a_n(t) < m/H'/n > e^{i\omega_{mn} t}$$

The term $-\frac{i}{\hbar} H' e^{i\omega_{mn} t}$ is called first order correction and $-\frac{i}{\hbar} \sum_{n \neq m} a_n(t) < m/\boldsymbol{H'}/\boldsymbol{n} > \boldsymbol{e^{i\omega_{mn} t}}$

Are called higher order corrections.

Assessment of first order correction

Now first order correction can be written as

$$\frac{\boldsymbol{d} a_m{}^1(t)}{\boldsymbol{dt}} = -\frac{i}{\hbar} H' e^{i\omega_{mn} t}$$

$$a_m{}^1(t) = -\frac{i}{\hbar} \int_0^t H' e^{i\omega_{mn} t} dt$$

This is the equation to use to compute transition probabilities for a general time dependent perturbation.

Example

Sinusoidal Perturbation $H' = 2V\, cos\omega t$

Solution

As first order correction is

$$a_m{}^1(t) = -\frac{i}{\hbar}\int_0^t H' e^{i\omega_{mn}t}dt$$

$$a_m{}^1(t) = -\frac{i}{\hbar}\int_0^t 2V\, cos\omega t e^{i\omega_{mn}t}dt$$

$$a_m{}^1(t) = -\frac{i}{\hbar}\int_0^t 2V\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)e^{i\omega_{mn}t}dt$$

$$a_m{}^1(t) = -\frac{i}{\hbar}\int_0^t V\left(e^{i(\omega_{mn}+\omega)t}+e^{i(\omega_{mn}-\omega)t}\right)dt$$

If $\omega_{mn} = \omega$ then term $e^{i(\omega_{mn}-\omega)t} = 1$ so

$$a_m{}^1(t) = -\frac{i}{\hbar}\int_0^t V e^{i(\omega_{mn}+\omega)t}dt$$

$$a_m{}^1(t) = -\frac{iV}{\hbar}\left|\frac{e^{i(\omega_{mn}+\omega)t}}{i(\omega_{mn}+\omega)}\right|_0^t = -\frac{iV}{\hbar}\left[\frac{e^{i(\omega_{mn}+\omega)t}-1}{i(\omega_{mn}+\omega)}\right]$$

$$a_m{}^1(t) = -\frac{iVe^{i(\omega_{mn}+\omega)t/2}}{\hbar}\left[\frac{e^{i(\omega_{mn}+\omega)t/2}-e^{-i(\omega_{mn}+\omega)t/2}}{i(\omega_{mn}+\omega)}\right]$$

$$a_m{}^1(t) = -\frac{iVe^{i(\omega_{mn}+\omega)t/2}}{\hbar}\left[\frac{2sin(\omega_{mn}+\omega)t/2}{i(\omega_{mn}+\omega)}\right]$$

Now probability of transition will be

$$P_n(t) = a_m{}^{1^*}(t)a_m{}^1(t) = |a_m{}^1(t)|^2 = \frac{V^2}{\hbar^2}\left[\frac{4sin^2(\omega_{mn}+\omega)t/2}{(\omega_{mn}+\omega)^2}\right]$$

$$P_n(t) = \frac{V^2}{\hbar^2}2\pi t\delta(\omega_{mn}+\omega) = \frac{V^2}{\hbar}2\pi t\delta\left((E_m - E_n + \omega\hbar\right)$$

Here δ is delta function.

Now transition rate will be

$$\frac{dP_n(t)}{dt} = \frac{V^2}{\hbar} 2\pi\delta\big((E_m - E_n + \omega\hbar\big)$$

This equation is also called Fermi Golden rule for transition.

Variational Principle

The **Variational Method** is a mathematical method that is used to approximately calculate the energy levels of difficult quantum systems. It can also be used to approximate the energies of a solvable system and then obtain the accuracy of the method by comparing the known and approximated energies. The Schrödinger equation can be solved exactly for our model systems including Particle in a Box (PIB), Harmonic Oscillator (HO), Rigid Rotor (RR), and the Hydrogen Atom. However, for systems that have more than one electron, the Schrödinger equation cannot be analytically solved and requires approximation like the variational method to be used. Suppose that we wish to solve the time-independent Schrödinger equation

$$H\psi = E\psi$$

Where H is a known (presumably complicated) time-independent Hamiltonian. Let ψ be a normalized trial solution to the above equation. The variational principle states, quite simply, that the ground-state energy, $\mathrm{E_o}$ is always less than or equal to the expectation value of H calculated with the trial wavefunction: i.e.,

$$E_o \leq < \psi/H/\psi >$$

Thus, by varying ψ until the expectation value of H is *minimized*; we can obtain an approximation to the wave function and energy of the ground-state.

Let us prove the variational principle. Suppose that the ψ_n and the E_n are the true eigenstates and eigenvalues of H: *i.e.*,

$$H\psi_n = E_n\psi_n$$

Furthermore, let

$$E_o < E_1 < E_2 < - -$$

So that ψ_o is the ground-state, ψ_1 the first excited state, *etc*. The ψ_n are assumed to be orthonormal: *i.e.*,

$$< \psi_n/\psi_m >= \delta_{nm}$$

If our trial wavefunction ψ is properly normalized then we can write

$$\psi = \sum_n c_n \psi_n$$

Where

$$\sum_n |c_n|^2 = 1$$

Now, the expectation value of H, calculated with , ψ takes the form

$$< \psi/H/\psi > = \left\langle \sum_n c_n \psi_n \middle| H \middle| \sum_n c_m \psi_m \right\rangle$$

$$= \sum_{n,m} c_n{}^* c_m \langle \psi_n | H | \psi_m \rangle$$

$$= \sum_{n,m} c_n{}^* c_m E_m \langle \psi_n | \psi_m \rangle = \sum_n E_n |c_n|^2$$

So, we can write above equation as

$$< \psi/H/\psi >= |c_o|^2 E_o + \sum_{n>0} E_n |c_n|^2$$

However, from above we can write

$$|c_o|^2 = 1 - \sum_{n>0} E_n |c_n|^2$$

Use value of $|c_o|^2$ in above equation we get

$$< \psi/H/\psi >= E_o + \sum_{n>0} (E_n - E_o)|c_n|^2$$

Now, the second term on the right-hand side of the above expression is *positive definite*, since $(E_n - E_o) > 0$ for all $n > 0$

Hence, we obtain the desired result

$$< \psi/H/\psi > \geq E_o$$

Or

$$\frac{< \psi/H/\psi >}{\langle \psi | \psi \rangle} \geq E_o$$

The denominator above is only necessary if the trial wave function needs to normalized. When given a trial wave function, sometimes the problem states if it is normalized or not. When forced to decide, if there is a constant in front of the function, that is usually assumed to be the normalization constant. If a constant is not present then there is no normalization constant and the denominator in above Equation is not necessary.

Suppose that we have found a good approximation, ψ_o , to the ground-state wavefunction. If ψ is a normalized trial wavefunction which is orthogonal to ψ_o (*i.e.*, $\langle \psi | \psi_o \rangle = 0$) then, by repeating the above analysis, we can easily demonstrate that

$$< \psi/H/\psi > \geq E_1$$

Thus, by varying ψ until the expectation value of H is *minimized*; we can obtain an approximation to the wave function and energy of the first excited state. Obviously, we can continue this process until we have approximations to all of the stationary Eigen states. Note, however, that the errors are clearly cumulative in this method, so that any approximations to highly excited states are unlikely to be very accurate. For this reason, the variational method is generally only used to calculate the ground-state and first few excited states of complicated quantum systems.

In variational method the first step is to choose the trail function ψ.

How to choose a Trial Wave function?

The trial function must have the characteristics that classify it as a wave function, i.e Continuous, etc. The trial function needs to have the same general shape as the true wave function. The trial function must have the same boundary conditions. To improve accuracy, the trial wave function can be represented as linear combinations of single trial wave functions.

Examples

1. We find the ground state energy for particle in a box

We know that for particle in a box of length L, the exact wave function and energy derived by Schrodinger's equation are

$$\psi(x) = A \sin \frac{\sqrt{2mE}}{\hbar} x$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

For n=1

$$E_1 = \frac{4.9\hbar^2}{mL^2}$$

We find this energy by using variational principle.

First we choose a trail wave function $\psi(x)$.

$$\psi(x) = Ax(L - x)$$

By definition of variational principle

$$\frac{< \psi/H/\psi >}{\langle \psi | \psi \rangle} \geq E_1$$

As Hamiltonian inside the box is

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

Now $< \psi/H/\psi >= \int_0^L \psi(x)^* (-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}) \psi(x) dx$

$$< \psi/H/\psi >= -\frac{\hbar^2}{2m}\int_0^L Ax(L-x)(\frac{d^2}{dx^2}) Ax(L-x)dx$$

$$< \psi/H/\psi >= -\frac{A^2\hbar^2}{2m}\int_0^L (xL - x^2)(\frac{d^2}{dx^2}) (xL - x^2)dx$$

$$< \psi/H/\psi >= -\frac{A^2\hbar^2}{2m}\int_0^L (xL - x^2)\,(-2)dx$$

$$< \psi/H/\psi >= -\frac{A^2\hbar^2}{2m}\left[\frac{Lx^2}{2} + \frac{x^3}{3}\right]_0^L$$

$$< \psi/H/\psi >= \frac{A^2\hbar^2}{m}\left[\frac{L^3}{2} + \frac{L^3}{3}\right]$$

$$< \psi/H/\psi >= \frac{5A^2\hbar^2L^3}{6m}$$

Now denominator

$$\langle \psi|\,\psi\rangle = \int_0^L Ax(L-x)\,Ax(L-x)dx$$

$$\langle \psi|\,\psi\rangle = A^2\int_0^L (xL - x^2)\,(xL - x^2)dx$$

$$\langle \psi|\,\psi\rangle = A^2\int_0^L (x^2L^2 + x^4 - 2x^3L)\,dx$$

$$\langle \psi|\,\psi\rangle = A^2\left[\frac{x^3L^2}{3} + \frac{x^5}{5} - 2\frac{x^4L}{4}\right]_0^L$$

$$\langle \psi|\,\psi\rangle = A^2\left[\frac{L^5}{3} + \frac{L^5}{5} - \frac{L^5}{2}\right]$$

$$\langle \psi|\,\psi\rangle = \frac{A^2L^5}{30}$$

So variational principle becomes

$$\frac{\frac{5A^2\hbar^2L^3}{6m}}{\frac{A^2L^5}{30}} \geq E_1$$

$$\frac{5\hbar^2}{mL^2} \geq E_1$$

$$E_1 \leq \frac{5\hbar^2}{mL^2}$$

So by variational principle the energy for n=1 is same as derived by Schrodinger's equation.

2. Now we find the ground state energy of harmonic oscillator by the use of variational principle

   The Hamiltonian of te harmonic oscillator is

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 x$$

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x$$

   Now we choose a trail wave function as

$$\psi_o = Ae^{-\alpha x^2}$$

   Now by definition of variational principle

$$E_o \leq \frac{<\psi/H/\psi>}{\langle\psi|\psi\rangle}$$

   Now

$$<\psi/H/\psi> = \left\langle Ae^{-\alpha x^2}\left| -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x \right| Ae^{-\alpha x^2}\right\rangle$$

$$<\psi/H/\psi> = A^2\int_{-\infty}^{+\infty} e^{-\alpha x^2}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x\right)e^{-\alpha x^2}dx$$

   By solving this integral we get

$$<\psi/H/\psi> = A^2\left[\frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\right]\left(\frac{\pi}{2\alpha}\right)^{\frac{1}{2}}$$

   Now

$$\langle\psi|\psi\rangle = A^2\int_{-\infty}^{+\infty} e^{-2\alpha x^2}dx$$

$$\langle\psi|\psi\rangle = A^2\left(\frac{\pi}{2\alpha}\right)^{\frac{1}{2}}$$

   So the variational principle

$$E_o \leq \frac{<\psi/H/\psi>}{\langle\psi|\psi\rangle} = \frac{A^2\left[\frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\right]\left(\frac{\pi}{2\alpha}\right)^{\frac{1}{2}}}{A^2\left(\frac{\pi}{2\alpha}\right)^{\frac{1}{2}}}$$

$$E_o \leq \left(\frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\right)$$

Now because there is a variational constant α, we need to minimize it. By putting

$$\frac{dE_o}{d\alpha} = 0$$

$$\frac{dE_o}{d\alpha} = \frac{d}{d\alpha}\left(\frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\right) = 0$$

$$\left(\frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2}\right) = 0$$

$$\alpha = \frac{m\omega}{2\hbar}$$

So

$$E_o \leq \left(\frac{\hbar^2 m\omega}{4m\hbar} + \frac{4\hbar^2 m\omega^2}{8m^2\omega^2}\right)$$

$$E_o \leq \frac{1}{2}\hbar\omega$$

If you notice, this is the exact equation for the Harmonic Oscillator ground state. We were able to find this by initially guessing a good wave function, and varying and minimizing the variational constant.

WKB Approximation

The WKB Approximation, named after scientists Wentzel–Kramers–Brillouin, is a method to approximate solutions to a time-independent linear differential equation or in this case, the Schrödinger Equation. Its principal applications are for calculating bound-state energies and tunneling rates through potential barriers. The WKB Approximation is most often applied to 1D problem, but also works for 3D spherically symmetric problems. As a general overview, the wave function is assumed to be an exponential function with either amplitude or phase taken to be slowly changing relative to the de Broglie wavelength λλ. It is then semi-classically expanded. The method is named after the physicists Wentzel, Kramers and Brillouin. It is sometimes called the WKBJ approximation, with Harold Jefreys' name tagged on the end to recognise the fact that he discovered before any of the other three. The main applications of the method are in estimating bound state energies and computing tunneling rates.

Applications in Quantum Mechanics: In quantum mechanics it is useful in

1. Calculating bound state energies (Whenever the particle cannot move to infinity)

2. Transmission probability through potential barriers.

Main idea: If potential ($\boldsymbol{x}$) is constant and energy E of the particle is $\boldsymbol{E} > \boldsymbol{V}$, then the particle wave function has the form $\psi\ x = Ae^{\pm ikx}$ where k = √$(2m(E-V))$ $\hbar$ (+) sign indicates : particle travelling to right (-) sign indicates : particle travelling to left General solution : Linear superposition of the two. The wave function is oscillatory, with fixed wavelength, λ = 2 . The amplitude (A) is fixed.

If V (x) is not constant, but varies slow in comparison with the wavelength λ in a way that it is essentially constant over many λ, then the wave function is practically sinusoidal, but wavelength and amplitude slowly change with x. This is the inspiration behind WKB approximation. In effect, it identifies two different levels of x-dependence: - rapid oscillations, modulated by gradual variation in amplitude and wavelength.

If E <V and V is constant then wave function is $\psi(x) = Ae^{\pm kx}$ where $k = \frac{\sqrt{2m(v-E)}}{\hbar}$

If V is not constant but varies slowly with1/k, the solution remains exponentially but both A and k are slowly varying function with x.

Failure of this idea: There is one place where this whole program is bound to fail, and that is in the immediate vicinity of a classical turning point, where $E \approx V$. For here (or 1/ κ)) goes to infinity and $V(x)$ can hardly be said to vary “slowly” in comparison. A proper handling of the turning points is the most difficult aspect of the WKB approximation, though the final results are simple to state and easy to implement.

The Classical Region Let's now solve the Schrödinger equation using WKB approximation

$$\frac{\mathrm{d}^2\psi(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi(\mathrm{x}) = 0$$

We can write above equation as

$$\frac{\mathrm{d}^2\psi(\mathrm{x})}{dx^2} + \frac{P^2}{\hbar^2}\psi(\mathrm{x}) = 0$$

Where $P^2 = 2m(E-V)$

is the classical formula for the momentum of a particle with total energy E and potential energy $V(x)$. Let's assume E > (x), so that P(x) is real. This is the classical region , as classically the particle is confined to this range of x.

The function ψ In general, ψ is some complex function; we can express it in terms of its amplitude $A(x)$, and its phase, $\phi(x)$ – both of which are real : $\psi\, x = A(x)e^{i\phi(x)}$

Solving the Schrödinger equation $\psi\ x$ = $(x)^{(x)}$ Using prime to denote the derivative with respect to x, we find: $d\psi/\ dx$ = (A '+$iA\phi$')$e\ i\phi$ and $d^2\psi\ /dx^2$ = [A ''+2iA 'ϕ ' + $iA\phi$ '' − $A\ \phi$ ' 2]$e^{i\phi}$ Putting all these into above equation , we get

$$A\ '' + 2iA\ '\phi\ ' + iA\phi\ '' - A\ \phi\ '\ 2 = -\ \mathrm{P}^2/\hbar^2\ A$$

Solving for real and imaginary parts we get,

$$A\ '' - A\ \phi\ '^2 = -\ \mathrm{P}^2/\hbar^2\ A$$

$$A\ '' = A\ [\phi\ '^2 - \mathrm{P}^2/\hbar^2\ ]$$

$$A''/\ A = \phi\ '^2 - \mathrm{P}^2/\hbar^2$$

The above equation cannot be solved in general, so we use WKB approximation: we assume amplitude A varies slowly, so that the A'' term is negligible. We assume that

$$A''/\ A << [\phi\ '^2 - \mathrm{P}^2/\hbar^2\ ].$$

Therefore, we neglect $A''/$, so we can write $\phi\ '^2 - \mathrm{P}^2/\hbar^2$=0

$$\phi\ '^2 = \mathrm{P}^2/\hbar^2$$

$$\phi' = \pm\frac{\mathrm{P}}{\hbar}$$

$$\phi = \pm\int \frac{\mathrm{P}}{\hbar}\mathrm{dx}$$

And from second equation, we get

$$2A'\phi' + A\phi'' = 0$$

$$(A^2\phi')' = 0$$

$$\mathrm{A} = \frac{\mathrm{c}}{\sqrt{\Phi'}}$$

Where c is real constant.

So we can write $\psi(x) = Ae^{\pm kx}$ as

$$\psi(x) = \frac{c}{\sqrt{P}} e^{\pm i \int \frac{\mathrm{P}}{\hbar} \mathrm{dx}}$$

$$\psi(x) = \frac{1}{\sqrt{P}} \left[c_1 e^{+i \int \frac{\mathrm{P}}{\hbar} \mathrm{dx}} + c_2 e^{-i \int \frac{\mathrm{P}}{\hbar} \mathrm{dx}} \right]$$

where C_1 and C_2 are constants.

Alternate approach In this approach, the wave function is expanded in powers of $\hbar$. Let, the wave function be: $\psi = Ae^{\,i\hbar(x)}$

Use this in Schrodinger's equation as

$$\frac{\mathrm{d}^2\psi(\mathrm{x})}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi(\mathrm{x}) = 0$$

$$\frac{\mathrm{d}^2\psi(\mathrm{x})}{dx^2} + K^2\psi(\mathrm{x}) = 0$$

$$\frac{\mathrm{d}^2 Ae^{i\hbar S}}{dx^2} + K^2 Ae^{i\hbar S} = 0$$

$$\left(\frac{dS}{dx}\right)^2 - i\hbar\frac{\mathrm{d}^2 S}{dx^2} - K^2\hbar^2 = 0$$

Expand S(x) in power of $\hbar$

$$S = S_0 + S_1\hbar + S_2\frac{\hbar^2}{2} + - - -$$

So above equation become

$$\left(\frac{dS_0}{dx}\right)^2 + \left(2\frac{dS_0}{dx}\frac{dS_1}{dx} - i\frac{d^2S_0}{dx^2}\right)\hbar - K^2\hbar^2 = 0$$

Neglecting higher powers of $\hbar$. For the above equation to be valid, the coefficient of each power of $\hbar$ must vanish separately, that is

$$\left(\frac{dS_0}{dx}\right)^2 - K^2\hbar^2 = 0$$

$$\left(\frac{dS_0}{dx}\right)^2 = K^2\hbar^2$$

$$\frac{dS_0}{dx} = \pm K\hbar$$

$$S_0 = \pm\int K\hbar dx$$

Similarly

$$\left(2\frac{dS_0}{dx}\frac{dS_1}{dx} - i\frac{d^2S_0}{dx^2}\right) = 0$$

Use value of S_0

$$\left(2\frac{\pm d\int K\hbar dx}{dx}\frac{dS_1}{dx} - i\frac{\pm d^2\int K\hbar dx}{dx^2}\right) = 0$$

$$\frac{dS_1}{dx} = \frac{i}{2K}\frac{dK}{dx}$$

$$S_1 = \frac{i}{2}\ln(K)$$

$$e^{iS_1} = \frac{1}{\sqrt{K}}$$

Since

$$\psi = Ae^{\frac{iS}{\hbar}}$$

Use value of S

$$\psi = Ae^{\frac{i(S_0+S_1\hbar)}{\hbar}} = Ae^{\frac{iS_0}{\hbar}}e^{iS_1}$$

$$\psi = \frac{A}{\sqrt{K}}e^{i(\pm\int K dx)}$$

For $E <$: the Schrodinger equation is ,

$$\frac{\mathrm{d}^2\psi(\mathrm{x})}{dx^2} - K^2\psi(\mathrm{x}) = 0$$

In the same way

$$\psi = \frac{B}{\sqrt{K}}e^{\pm\int K dx}$$

Validity of WKB solution

The zeroeth order WKB solution is:

$$\psi = \frac{A}{\sqrt{K}}e^{i(\pm\int K dx)}$$

Only + term will be

$$\psi = \frac{A}{\sqrt{K}}e^{i(\int K dx)}$$

$$\frac{d\psi}{dx} = iK\psi$$

$$\frac{d^2\psi}{dx^2} = i\frac{dK}{dx}\psi + (iK)^2\psi$$

$$\frac{d^2\psi}{dx^2} + K^2\psi + i\frac{dK}{dx}\psi = 0$$

But our equation is

$$\frac{d^2\psi}{dx^2} + K^2\psi = 0$$

Which means that the factor

$$\frac{dK}{dx} \ll K^2$$

This implies that

$$\frac{1}{K}\frac{dK}{dx} \ll K$$

This shows K is varying slowly with x. This is the Validity condition for WKB approximation.

CHAPTER 9

RELATIVISTIC QUANTUM MECHANICS

In physics, relativistic quantum mechanics (RQM) is applicable to massive particles propagating at all velocities up to those comparable to the speed of light *c*, and can accommodate mass less. The theory has application in high energy physics, particle physics and accelerator physics, as well as atomic physics, chemistry and condensed matter physics. We discuss two important Equations which deals the relativistic quantum Mechanics.

1. Klein-Gordon equation

The Schrödinger Equation only describes particles in the non-relativistic limit. To describe the particles at particle colliders we need to incorporate special relativity.

According to Einstein's special theory of relativity

$$E^2 = P^2C^2 + {m_0}^2C^4 \text{-------- (1)}$$

Here E is total energy ,P is momentum ,C is speed of light and m_o is rest mass of the body.

In quantum Mechanics

$$E = i\hbar\frac{\partial}{\partial t} \qquad and \qquad P = -i\hbar\nabla$$

Substitute these values in equation 1

$$(i\hbar\frac{\partial}{\partial t})^2 = (-i\hbar\nabla)^2C^2 + {m_0}^2C^4$$

Simplify and multiply by wave function $\psi(r,t)$

$$-\hbar^2\frac{\partial^2\psi(r,t)}{\partial t^2} = -C^2\hbar^2\nabla^2\ \psi(r,t) + {m_0}^2C^4\ \psi(r,t)$$

$$\frac{\partial^2\psi(r,t)}{\partial t^2} = -C^2\nabla^2\ \psi(r,t) + \frac{{m_0}^2C^4}{\hbar^2}\ \psi(r,t)$$

$$\nabla^2\ \psi(r,t) - \frac{1}{C^2}\frac{\partial^2\psi(r,t)}{\partial t^2} + \frac{{m_0}^2C^2}{\hbar^2}\ \psi(r,t) = 0$$

$$\left[\nabla^2\ -\frac{1}{C^2}\frac{\partial^2}{\partial t^2}\right]\psi(r,t) + k^2\ \psi(r,t) = 0$$

$$(\square^2 + k^2)\ \psi(r,t) = 0$$

This is Kelien-Gordon Equation. Here $\square^2 = \nabla^2\ -\frac{1}{C^2}\frac{\partial^2}{\partial t^2}$ is called d'Alembert operator and $k^2 = \frac{{m_0}^2C^2}{\hbar^2}$.

Kelien- Gordon equation is a second order differential equation, its solution is

$$\psi(r,t) = Ae^{\frac{i(Pr-Et)}{\hbar}}$$

That represents a plane wave. If we put this $\psi(r,t)$ solution in Kelien-Gordon equation we get

$$E = \pm\sqrt{P^2C^2 + {m_0}^2C^4}$$

+ Energy represent particle but – Energy gives a strange result that if momentum of particle increases, its energy decreases.

Limitations of Kelien-Gordon Equation

Following the limitations of Kelien-Gordon equation

1. This equation is only for spinless particles.
2. Klein-Gordon equation has both positive and negative energy solutions.
3. Klein-Gordon equation is not first order in time derivative, while Schrodinger's equation has first order time derivative. So for Kelien-Gordon equation we have to measure both $\psi(r,t)$ and $\frac{d\psi(r,t)}{dt}$ at t=0
4. Density ρ is not positive definite for Kelien-Gordon equation.

Equation of Continuity from Kelien-Gordon equation

As Kelien-Gordon equation is

$$\frac{-\hbar^2}{C^2}\frac{\partial^2\psi(r,t)}{\partial t^2} = -\hbar^2\nabla^2\ \psi(r,t) + {m_0}^2C^2\ \psi(r,t)\text{--------(a)}$$

Multiply by ψ^*

$$\frac{-\hbar^2\psi^*}{C^2}\frac{\partial^2\psi(r,t)}{\partial t^2} = -\hbar^2\psi^*\nabla^2\ \psi(r,t) + {m_0}^2C^2\ \psi^*\psi(r,t)\text{------(b)}$$

Now take the complex conjugate of equation a and multiply with ψ

$$\frac{-\hbar^2\psi}{C^2}\frac{\partial^2\psi^*(r,t)}{\partial t^2} = -\hbar^2\psi\nabla^2\ \psi^*(r,t) + {m_0}^2C^2\ \psi\psi^*(r,t)\text{------(c)}$$

Subtract equations b and c

$$\frac{-\hbar^2\psi^*}{C^2}\frac{\partial^2\psi(r,t)}{\partial t^2} + \frac{\hbar^2\psi}{C^2}\frac{\partial^2\psi^*(r,t)}{\partial t^2} = -\hbar^2\psi^*\nabla^2\ \psi(r,t) + \hbar^2\psi\nabla^2\ \psi^*(r,t)$$

$$\frac{-\hbar^2}{C^2}\left(\psi^*\frac{\partial^2\psi(r,t)}{\partial t^2} - \frac{\psi\partial^2\psi^*(r,t)}{\partial t^2}\right) = -\hbar^2\left(\psi^*\nabla^2\ \psi(r,t) - \psi\nabla^2\ \psi^*(r,t)\right)$$

$$\frac{-\hbar^2}{C^2}\left(\psi^*\frac{\partial^2\psi}{\partial t^2} - \frac{\psi\partial^2\psi^*}{\partial t^2}\right) + \hbar^2(\psi^*\nabla^2\ \psi - \psi\nabla^2\ \psi^*) = 0$$

$$\frac{-\hbar^2}{C^2}\frac{\partial}{\partial t}\left(\psi^*\frac{\partial\psi}{\partial t} - \psi\frac{\partial\psi^*}{\partial t}\right) + \hbar^2\nabla(\ \psi^*\nabla\psi - \psi\nabla\ \psi^*) = 0$$

$$\frac{\partial}{\partial t}\left[\frac{i\hbar}{2m_oC^2}\left(\psi^*\frac{\partial\psi}{\partial t}-\psi\frac{\partial\psi^*}{\partial t}\right)\right]+\nabla\left[\frac{\hbar}{2m_oi}(\psi^*\nabla\psi-\psi\nabla\psi^*)\right]=0$$

$$\frac{\partial\rho}{\partial t}+\nabla.\mathrm{J}=0$$

This is equation of continuity. Here $\rho=\frac{i\hbar}{2m_oC^2}\left(\psi^*\frac{\partial\psi}{\partial t}-\psi\frac{\partial\psi^*}{\partial t}\right)$ and $\mathrm{J}=\frac{\hbar}{2m_oi}(\psi^*\nabla\psi-\psi\nabla\psi^*)$

Are the charge density and current density respectively. We can see that the integral of the density ρ over all space is conserved. However, is not positively definite. Therefore, we can neither interpret as the particle probability density nor can we interpret J as the particle current. The appropriate interpretation is charge density $e\rho$ for and electric current for eJ since charge density and electric current can be either positive or negative.

Schrödinger's equation from Kelien-Gordon equation

In non relativistic limit Kelien-Gordon equation goes to Schrodinger's equation. For non relativistic particle V<<C and p<<m_oC.

We have

$$E=\sqrt{P^2C^2+{m_0}^2C^4}$$

$$E=m_0C^2\left(1+\frac{P^2}{{m_0}^2C^2}\right)^{\frac{1}{2}}$$

$E=m_0C^2\left(1+\frac{P^2}{2{m_0}^2C^2}\right)$ Binomial expension.Neglect higher terms.

$$E=m_0C^2+\frac{P^2}{2m_0}$$

This equation shows relativistic energy differs from classical energy $\frac{P^2}{2m_0}$by factor m_0C^2.

Now the solution of Kelien-Gordon equation is

$$\psi(r,t)=Ae^{\frac{i(Pr-Et)}{\hbar}}$$

We can write it as

$$\psi(r,t) = Ae^{\frac{i(Pr)}{\hbar}} e^{\frac{-i(m_0C^2t)}{\hbar}}$$

$$\psi(r,t) = \psi_o e^{\frac{-i(m_0C^2t)}{\hbar}}$$

Use this value in Kelien-Gordon equation

$$-\hbar^2 \frac{\partial^2 \psi_o e^{\frac{-i(m_0C^2t)}{\hbar}}}{\partial t^2} = -C^2\hbar^2\nabla^2\ \psi_o e^{\frac{-i(m_0C^2t)}{\hbar}} + {m_0}^2C^4\,\psi_o e^{\frac{-i(m_0C^2t)}{\hbar}}$$

$$-\hbar^2 \frac{\partial^2 \psi_o}{\partial t^2} e^{\frac{-i(m_0C^2t)}{\hbar}} + 2\frac{\partial \psi_o}{\partial t}(i(m_0\hbar C^2)) e^{\frac{-i(m_0C^2t)}{\hbar}} - \hbar^2 \left(\frac{-i(m_0C^2)}{\hbar}\right)^2 \psi_o e^{\frac{-i(m_0C^2t)}{\hbar}}$$

$$= -C^2\hbar^2\nabla^2\ \psi_o e^{\frac{-i(m_0C^2t)}{\hbar}} + {m_0}^2C^4\,\psi_o e^{\frac{-i(m_0C^2t)}{\hbar}}$$

$$-\hbar^2 \frac{\partial^2 \psi_o}{\partial t^2} e^{\frac{-i(m_0C^2t)}{\hbar}} + 2\frac{\partial \psi_o}{\partial t}(im_0\hbar C^2) e^{\frac{-i(m_0C^2t)}{\hbar}^2} + {m_0}^2C^4\,\psi_o e^{\frac{-i(m_0C^2t)}{\hbar}}$$

$$= -C^2\hbar^2\nabla^2\ \psi_o e^{\frac{-i(m_0C^2t)}{\hbar}} + {m_0}^2C^4\,\psi_o e^{\frac{-i(m_0C^2t)}{\hbar}}$$

$$-\hbar^2 \frac{\partial^2 \psi_o}{\partial t^2} + 2(im_0\hbar C^2)\frac{\partial \psi_o}{\partial t} = -C^2\hbar^2\nabla^2\ \psi_o$$

$$\frac{-\hbar^2}{2m_0C^2}\frac{\partial^2 \psi_o}{\partial t^2} + i\hbar\frac{\partial \psi_o}{\partial t} = \frac{-C^2}{2m_0C^2}\hbar^2\nabla^2\ \psi_o$$

Term $\frac{-\hbar^2}{2m_0C^2}\frac{\partial^2 \psi_o}{\partial t^2}$ is very small we neglect it.

$$i\hbar\frac{\partial \psi_o}{\partial t} = \frac{-\hbar^2}{2m_0}\nabla^2\ \psi_o$$

$$\frac{-\hbar^2}{2m_0}\nabla^2\,\psi_o = i\hbar\frac{\partial \psi_o}{\partial t}$$

$$H\psi_o = E\psi_o$$

This is Schrodinger's equation.

2. Dirac equation

Dirac equation is a relativistic wave equation derived by British physicist Paul Dirac in 1928. In its free form, or including electromagnetic interactions, it describes all Spin ½ massive particles such as electrons and quarks for which parity is a symmetry. It is consistent with both the principles of quantum mechanics and the theory of special relativity, and was the first theory to account fully for special relativity in the context of quantum mechanics. The equation also implied the existence of a new form of matter, *antimatter*,

Apparently, Schrodinger tried out Klein equation before proceeding with his non-relativistic equations, but dropped it seeing many problems and never published it… This equation was discarded in the community as faulty… In addition, it did not leave any room for spin states, while electrons and protons were known to have spin ½. Motivated by these problems, Dirac set to find another relativistic quantum mechanical equation…. What happened next is: in 1928 Dirac finds a linear equation; it describes fermions; however, it still has negative energy solutions… in 1930 Dirac interprets the negative energy solutions as holes in the "sea" (now commonly referred as Dirac sea) that must behave as opposite charge particles. In 1932 Positrons are found. In 1934 Pauli and Weisskopf showed that the second problem was not really a problem. Since relativistic quantum mechanical equation had to allow for creation and annihilation of particles, the integral probability did not have to stay constant, anymore. The conserved ρ was reinterpreted as charge density, which, of course, could take negative values.

Now the Einstein's equation is

$$E^2 = P^2C^2 + {m_0}^2C^4 \text{-------- (1)}$$

We arrange this equation

$$\frac{E^2}{C^2} = P^2 + {m_0}^2C^2$$

$$\frac{E^2}{C^2} - P^2 = {m_0}^2 C^2$$

$$\left(\frac{E}{C} + P\right)\left(\frac{E}{C} - P\right) = {m_0}^2 C^2$$

Replace $P = \sigma . P$

$$\left(\frac{E}{C} + \sigma . P\right)\left(\frac{E}{C} - \sigma . P\right) = {m_0}^2 C^2$$

In quantum Mechanics

$$E = i\hbar\frac{\partial}{\partial t} \qquad and \qquad P = -i\hbar\nabla$$

So above equation becomes

$$\left(i\hbar\frac{\partial}{\partial Ct} - i\hbar\sigma . \nabla\right)\left(i\hbar\frac{\partial}{\partial Ct} + i\hbar\sigma . \nabla\right) = {m_0}^2 C^2$$

As$Ct = x_o$ $$\left(i\hbar\frac{\partial}{\partial x_o} - i\hbar\sigma . \nabla\right)\left(i\hbar\frac{\partial}{\partial x_o} + i\hbar\sigma . \nabla\right) = {m_0}^2 C^2$$

Multiply both sides by ψ

$$\left(i\hbar\frac{\partial}{\partial x_o} - i\hbar\sigma . \nabla\right)\left(i\hbar\frac{\partial}{\partial x_o} + i\hbar\sigma . \nabla\right)\psi = {m_0}^2 C^2 \psi \text{ -------(2)}$$

Now we define

$$\psi_1 = \psi \quad \text{And} \quad \psi_2 = \frac{1}{m_0 C}\left(i\hbar\frac{\partial}{\partial x_o} - i\hbar\sigma . \nabla\right)\psi_1$$

So equation 2 becomes $$\left(i\hbar\frac{\partial}{\partial x_o} - i\hbar\sigma . \nabla\right)\left(i\hbar\frac{\partial}{\partial x_o} + i\hbar\sigma . \nabla\right)\psi_1 = {m_0}^2 C^2 \psi_1 \text{-------(3)}$$

$$\left(i\hbar\frac{\partial}{\partial x_o} + i\hbar\sigma . \nabla\right) m_0 C\psi_2 = {m_0}^2 C^2 \psi_1 \text{------(4)}$$

$$\left(i\hbar\frac{\partial}{\partial x_o} + i\hbar\sigma . \nabla\right)\psi_2 = m_0 C\psi_1 \text{-----(5)}$$

$$\left(i\hbar\frac{\partial}{\partial x_o} - i\hbar\sigma . \nabla\right)\psi_1 = m_0 C\psi_2 \text{ -----(6)}$$

Now we re-write the equation 5 and 6

$$\left(i\hbar\frac{\partial}{\partial x_o}+i\hbar\sigma.\nabla\right)\psi_2-m_0C\psi_1=0\text{-----(7)}$$

$$\left(i\hbar\frac{\partial}{\partial x_o}-i\hbar\sigma.\nabla\right)\psi_1-m_0C\psi_2=0\text{ -----(8)}$$

Take the sum and difference of equation 7 and 8

$$i\hbar\frac{\partial}{\partial x_o}(\psi_2-\psi_1)+i\hbar\sigma.\nabla(\psi_2+\psi_1)-m_0C(\psi_2+\psi_1)=0\text{------(9)}$$

And Difference

$$i\hbar\frac{\partial}{\partial x_o}(\psi_2+\psi_1)+i\hbar\sigma.\nabla(\psi_2-\psi_1)+m_0C(\psi_2-\psi_1)=0\text{------(10)}$$

Put $\psi_2+\psi_1=\psi_A$ and $\psi_2-\psi_1=\psi_B$ in equations 9 and 10

$$i\hbar\frac{\partial}{\partial x_o}\psi_B+i\hbar\sigma.\nabla\psi_A-m_0C\psi_A=0$$

$$-i\hbar\sigma.\nabla\psi_A-i\hbar\frac{\partial}{\partial x_o}\psi_B+m_0C\psi_A=0\text{ -------(11)}$$

$$i\hbar\frac{\partial}{\partial x_o}\psi_A+i\hbar\sigma.\nabla\psi_B+m_0C\psi_B=0$$

$$i\hbar\sigma.\nabla\psi_B+i\hbar\frac{\partial}{\partial x_o}\psi_A+m_0C\psi_B=0\text{ -------(12)}$$

In matrix form

$$\begin{pmatrix}-i\hbar\frac{\partial}{\partial x_o} & -i\hbar\sigma.\nabla\\ i\hbar\sigma.\nabla & i\hbar\frac{\partial}{\partial x_o}\end{pmatrix}\begin{pmatrix}\psi_A\\ \psi_B\end{pmatrix}+m_0C\begin{pmatrix}\psi_A\\ \psi_B\end{pmatrix}=0\text{------(13)}$$

Here ψ_A and ψ_B two components spinors that is these have totally 4 components. Now

$$\begin{pmatrix}-i\hbar\frac{\partial}{\partial x_o} & -i\hbar\sigma.\nabla\\ i\hbar\sigma.\nabla & i\hbar\frac{\partial}{\partial x_o}\end{pmatrix}=\hbar\left[\begin{pmatrix}0 & -i\sigma.\nabla\\ i\sigma.\nabla & 0\end{pmatrix}+\begin{pmatrix}\frac{\partial}{\partial x_o} & 0\\ 0 & -\frac{\partial}{\partial x_o}\end{pmatrix}\right]$$

$$\begin{pmatrix} -i\hbar\frac{\partial}{\partial x_o} & -i\hbar\sigma.\nabla \\ i\hbar\sigma.\nabla & i\hbar\frac{\partial}{\partial x_o} \end{pmatrix} = \hbar\left[\begin{pmatrix} 0 & -i\sigma_{\mathrm{i}} \\ i\sigma_{\mathrm{i}} & 0 \end{pmatrix}\frac{\partial}{\partial x_{\mathrm{i}}} + \begin{pmatrix} \frac{\partial}{\partial x_4} & 0 \\ 0 & -\frac{\partial}{\partial x_4} \end{pmatrix}\right]$$

$$\begin{pmatrix} -i\hbar\frac{\partial}{\partial x_o} & -i\hbar\sigma.\nabla \\ i\hbar\sigma.\nabla & i\hbar\frac{\partial}{\partial x_o} \end{pmatrix} = \hbar\left[\begin{pmatrix} 0 & -i\sigma_{\mathrm{i}} \\ i\sigma_{\mathrm{i}} & 0 \end{pmatrix}\frac{\partial}{\partial x_{\mathrm{i}}} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\frac{\partial}{\partial x_4}\right]$$

$$\begin{pmatrix} -i\hbar\frac{\partial}{\partial x_o} & -i\hbar\sigma.\nabla \\ i\hbar\sigma.\nabla & i\hbar\frac{\partial}{\partial x_o} \end{pmatrix} = \hbar\left[\gamma_{\mathrm{i}}\frac{\partial}{\partial x_{\mathrm{i}}} + \gamma_4\frac{\partial}{\partial x_4}\right]$$

$$\begin{pmatrix} -i\hbar\frac{\partial}{\partial x_o} & -i\hbar\sigma.\nabla \\ i\hbar\sigma.\nabla & i\hbar\frac{\partial}{\partial x_o} \end{pmatrix} = \hbar\gamma_{\mu}\frac{\partial}{\partial x_{\mu}}$$

Here $\gamma_{\mathrm{i}} = \begin{pmatrix} 0 & -i\sigma_{\mathrm{i}} \\ i\sigma_{\mathrm{i}} & 0 \end{pmatrix}$ and $\gamma_4 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

So equation 13 becomes

$$\hbar\gamma_{\mu}\frac{\partial}{\partial x_{\mu}}\begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} + m_0 C\begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = 0$$

$$\hbar\gamma_{\mu}\frac{\partial\psi}{\partial x_{\mu}} + m_0 C\psi = 0$$

This is dirac equaton.Here $\psi = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}$

$\psi_1$and ψ_2 are the wave functions of particle with spin clockwise and anticlock wise.While $\psi_3$and ψ_4 are the wave functions of anti-particle with spin clockwise and anticlock wise.

The gamma matrices are 4 by 4 matrices operating in this spinor space.

$$\gamma_1 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}, \gamma_2 = \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$$

$$\gamma_3 = \begin{pmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \\ i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{pmatrix}, \gamma_4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

Solution of the dirac equation for the particle in rest i.e P=0 will be

$$\hbar\gamma_\mu \frac{\partial}{\partial x_\mu}\begin{pmatrix}\psi_A \\ \psi_B\end{pmatrix} + m_0 C \begin{pmatrix}\psi_A \\ \psi_B\end{pmatrix} = 0$$

$$\hbar = C = 1 \; for \; natural \; units$$

$$\gamma_\mu \frac{\partial}{\partial x_\mu}\begin{pmatrix}\psi_A \\ \psi_B\end{pmatrix} = -m_0 \begin{pmatrix}\psi_A \\ \psi_B\end{pmatrix}$$

$$i\gamma_4 \frac{\partial}{\partial \mathrm{t}}\begin{pmatrix}\psi_A \\ \psi_B\end{pmatrix} = -m_0 \begin{pmatrix}\psi_A \\ \psi_B\end{pmatrix}$$

$$i\frac{\partial}{\partial \mathrm{t}}\begin{pmatrix}1 & 0 \\ 0 & -1\end{pmatrix}\begin{pmatrix}\psi_A \\ \psi_B\end{pmatrix} = -m_0 \begin{pmatrix}\psi_A \\ \psi_B\end{pmatrix}$$

It has two positive energy solutions that correspond to two spin states of spin-½ particles

$$\psi_A = \mathrm{e}^{-i\mathrm{mt}}\begin{pmatrix}1 \\ 0\end{pmatrix} \text{ And } \psi_B = \mathrm{e}^{-i\mathrm{mt}}\begin{pmatrix}0 \\ 1\end{pmatrix}$$

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The Conserved Probability Current OR Equation of Continuity

As Dirac equation is

$$\hbar\gamma_\mu \frac{\partial\psi}{\partial x_\mu} + m_0 C\psi = 0 \text{------(a)}$$

We take the Hermitain conjugate of this equation instead of complex conjugate. Because γ matrices are Hermiatian.

$$\frac{\partial\psi^{\dagger}}{\partial x_{\mu}{}^{*}}\gamma_{\mu}+\frac{m_0C}{\hbar}\psi^{\dagger}=0$$

The complex conjugate does nothing to the spatial component of x_{μ} but only will change the sign of 4th component.

We split the above equation in spatial and time components as

$$\frac{\partial\psi^{\dagger}}{\partial x_{\mathrm{k}}}\gamma_{\mathrm{k}}+\frac{\partial\psi^{\dagger}}{\partial x_{4}{}^{*}}\gamma_{4}+\frac{m_0C}{\hbar}\psi^{\dagger}=0$$

Multiply this equation by γ_4 on right.

$$\frac{\partial\psi^{\dagger}}{\partial x_{\mathrm{k}}}\gamma_{\mathrm{k}}\gamma_{4}-\frac{\partial\psi^{\dagger}}{\partial x_{4}{}^{*}}\gamma_{4}\gamma_{4}+\frac{m_0C}{\hbar}\psi^{\dagger}\gamma_{4}=0$$

$$-\frac{\partial\psi^{\dagger}\gamma_{4}}{\partial x_{\mathrm{k}}}\gamma_{\mathrm{k}}-\frac{\partial\psi^{\dagger}\gamma_{4}}{\partial x_{4}{}^{*}}\gamma_{4}+\frac{m_0C}{\hbar}\psi^{\dagger}\gamma_{4}=0$$

Put $\psi^{\dagger}\gamma_{4}=\bar{\psi}$

$$-\frac{\partial\bar{\psi}}{\partial x_{\mathrm{k}}}\gamma_{\mathrm{k}}-\frac{\partial\bar{\psi}}{\partial x_{4}{}^{*}}\gamma_{4}+\frac{m_0C}{\hbar}\bar{\psi}=0$$

$$\Rightarrow-\frac{\partial\bar{\psi}}{\partial x_{\mu}}\gamma_{\mu}+\frac{m_0C}{\hbar}\bar{\psi}=0\text{--------(b)}$$

Now multiply equation a with $\bar{\psi}$ from left and equation b with $\psi$from right and subtract.

Equation a $$\bar{\psi}\gamma_{\mu}\frac{\partial\psi}{\partial x_{\mu}}+\frac{m_0C}{\hbar}\bar{\psi}\psi=0$$

Equation a $$-\frac{\partial\bar{\psi}}{\partial x_{\mu}}\gamma_{\mu}\psi+\frac{m_0C}{\hbar}\bar{\psi}\psi=0$$

Subtraction $$\bar{\psi}\gamma_{\mu}\frac{\partial\psi}{\partial x_{\mu}}+\frac{m_0C}{\hbar}\bar{\psi}\psi+\frac{\partial\bar{\psi}}{\partial x_{\mu}}\gamma_{\mu}\psi-\frac{m_0C}{\hbar}\bar{\psi}\psi=0$$

$$\bar{\psi}\gamma_\mu \frac{\partial \psi}{\partial x_\mu} + \frac{\partial \bar{\psi}}{\partial x_\mu}\gamma_\mu \psi = 0$$

$$\frac{\partial}{\partial x_\mu}\left(\bar{\psi}\gamma_\mu \psi\right) = 0$$

$$\frac{\partial}{\partial x_\mu} J_\mu = 0$$

This is Conserved Probability Current. Where $J_\mu = \left(\bar{\psi}\gamma_\mu \psi\right)$ is current density. In above equation 4th component of the current will be *i*C time the probability which gives $\frac{\partial \rho}{\partial t}$. That is

$$\frac{\partial}{\partial x_k} J_k + \frac{\partial}{\partial x_4} J_4 = 0$$

$$\frac{\partial J_k}{\partial x_k} + \frac{\partial \rho}{\partial t} = 0$$